Constraining the geothermal parameters of *in situ* Rb–Sr dating on Proterozoic shales and ~~its~~their subsequent applications

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Abstract Recent developments in tandem laser ablation-mass spectrometer technology have ~~been shown to be capable of~~demonstrated capacity for separating parent and daughter isotopes of the same mass online. As a result, beta decay chronometers can now be applied to the geological archive *in situ* as opposed to through traditional whole-rock digestions. One novel application of this technique is the *in situ* Rb–Sr dating ~~on~~of Proterozoic shales that are dominated by authigenic clays such as illite. This method can provide a depositional window for shales by differentiating signatures of early diagenetic processes versus late-stage secondary alteration. However, the hydrothermal sensitivity of the Rb–Sr isotopic system across geological timescales in shale-hosted clay minerals is not well understood. As such, we dated the Mesoproterozoic Velkerri Formation from the Altree 2 well in the Beetaloo Sub-basin (greater McArthur Basin~~)~~), northern Australia, using ~~*in situ* Rb–Sr geochronology and~~ this approach. We then constrained ~~its~~ thermal history of these units using common hydrocarbon maturity indicators~~. Furthermore, thermal modelling~~, and modelled effects of contact heating due to the intrusion of the Derim Derim Dolerite ~~intrusion that crosscut the unit was also constructed to help define these parameters~~.

In situ Rb–Sr dating of mature, oil-prone shales in the diagenetic zone from the Velkerri Formation ~~in this study~~ yielded ages of ~~1470 ± 102~~1448 ± 81 Ma, ~~1457 ± 29~~1434 ± 19 Ma, and 1421 ± ~~152~~139 Ma. These results agree with previous Re–Os dating of the unit and are interpreted as recording the timing of an early diagenetic event soon after deposition. Conversely, overmature, gas-prone shales in the anchizone sourced from ~~stratigraphically~~ deeper within the ~~same~~ borehole ~~and succession~~ were dated at ~~1318 ± 105~~1322 ± 93 Ma and ~~1332 ± 67~~1336 ± 40 Ma. These ages are younger than the expected depositional window for the Velkerri Formation. Instead, they are consistent with the

Commented [DS1]: Reviewer 1: "Hydrothermal" implies interaction of rocks with hot fluids generated from a cooling magma – better change to "thermal sensitivity".

Commented [DS2R1]: "Hydrothermal" implies interaction of rocks with hot fluids generated from a cooling magma – better change to "thermal sensitivity".

Commented [DS3]: Reviewer 1: Worthy to say that the study site is located in Australia…

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age of the Derim Derim Dolerite mafic intrusion intersected 800 m below the ~~unit. Computational~~Velkerri Formation. Thermal modelling suggests that a single intrusion of 75 m thickness would have been capable of producing a significant hydrothermal perturbation radiating from the sill top. The intrusion width proposed by this model is consistent with similar Derim Derim Dolerite sill thicknesses found elsewhere in the McArthur Basin. The extent of the hydrothermal aureole induced by this intrusion coincide with the ~~point~~window in which kerogen from the Velkerri Formation becomes overmature. As a result, the mafic intrusion intersected here is interpreted to have ~~driven the~~caused kerogen in these shales ~~into~~to enter the gas window, induced fluids that mobilise trace elements and ~~resetting~~reset the Rb–Sr chronometer. Consequently, we propose that the Rb–Sr chronometer in shales may be sensitive to temperatures of ca. ~~110~~120°C in hydrothermal reactions but can withstand temperatures of more than 190°C in ~~purely~~ thermal systems not dominated by fluids. Importantly, this study demonstrates a framework for the combined use of *in situ* Rb–Sr dating and kerogen maturation indicators to help reveal the thermochronological history of Proterozoic sedimentary basins. As such, this approach can be a powerful tool for identifying the hydrocarbon potential of source rocks in similar geological settings.

1 Introduction

The Rb–Sr isotopic system has historically been one of the most powerful dating tools in Earth science. Rb is abundant in K-rich minerals such as micas, clays, and K-feldspar, and these minerals are commonly found in a wide range of geological settings (Simmons, 1998). ~~As such,~~Therefore it is an effective technique to date processes such as igneous ~~emplacements~~emplacement, metamorphism, sedimentation, clay authigenesis, and hydrothermal alteration when these phases can be differentiated (Nebel, 2014). Its long half-life also makes it applicable to date events as early as the infant stages of our solar system (Minster et al., 1979; Nebel et al., 2011; Papanastassiou and Wasserburg, 1970). Traditionally, the application of this method required an arduous process of column chromatography to chemically separate the parent (^{87}Rb) and daughter (^{87}Sr) isotopes and avoid isobaric interference between the two elements (Charlier et al., 2006; Dickin, 2018; Faure, 1977; Hahn et al., 1943; Hahn and Walling, 1938; Yang et al., 2010). Alas, this approach has historically been expensive, time consuming, and results in the loss of the genetic relationships between the minerals analysed~~ which caused~~, causing the technique to lose its popularity in recent years (Nebel, 2014).

Commented [DS7]: Reviewer 1: Worthy to say that distinctions between detrital and authigenic (plus resetting events) mineral phases must be made.

Commented [DS8R7]: Done.

Recent advancements in tandem laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS/MS) and similar instruments have revitalised the use of Rb–Sr by allowing them to be applied *in situ* (Bevan et al., ~~2021~~2021b;

Commented [DS9]: Reviewer 1: instruments // techniques

Commented [DS10R9]: 'Instruments' is correct, as this is said in reference to the application of similar methods using different instruments such as a Multi-Collector.

Gorojovsky and Alard, 2020; Hogmalm et al., 2017; Redaa et al., 2021a; Yim et al., 2021; Zack and Hogmalm, 2016). ~~A reactive gas~~Reactive gasses such as N_2O and SF_6 can be introduced into a reaction cell between quadrupoles in an LA-ICP-MS/MS system, which permits the online separation of ^{87}Sr from ^{87}Rb through the measurement of the mass shifted Sr reaction product (Hogmalm et al., 2017; Redaa et al., 2021a; Zack and Hogmalm, 2016). ~~The method~~This allows for a more rapid and economic analysis time, as well as the ability to preserve petrographic relationships during these analyses. Consequently, secondary input of Rb or Sr from inclusions, zonation, alteration, and detritus can be isolated, resulting in a better understanding of the geochronological results. However, it should be noted that nm or µm sized mineral intergrowths of different origins still provide challenges when large spot sizes are used. The application of similar setups with other beta-decay dating systems have also yielded promising results (Bevan et al., 2021a; Brown et al., 2022; Gorojovsky and Alard, 2020b; Harrison et al., 2010; Hogmalm et al., 2019; Ribeiro et al., 2021; Rösel and Zack, 2022; Scheiblhofer et al., 2022; Simpson et al., 2021; Simpson et al., 2022; Tamblyn et al., 2021).

Commented [DS11]: Reviewer 1: Define "reactive gas".

Commented [DS12R11]: Done.

Commented [DS13]: Reviewer 1: 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.

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~~As a result~~Hence, the *in situ* Rb–Sr dating method can now be used very similarly to laser ablation U–Pb dating, where age information can be obtained reliably, rapidly, and cheaply. ~~Datable minerals for this method are often macroscopically visible and abundant, avoiding the need for extensive mineral separation commonly needed for U–Pb geochronology (Zack and Hogmalm, 2016).~~ In addition, the initial ^{87}Sr/^{86}Sr ratio from the calculated isochron and the elemental data concurrently collected with the Rb and Sr isotopes can fingerprint the geochemical nature of the samples analysed (Li et al., 2020; Redaa et al., 2021b; Subarkah et al., 2021; Tamblyn et al., 2020). This approach ~~have~~has been shown to be capable of dating paragenetic sequences in deformation structures (Armistead et al., 2020; Tillberg et al., 2020), hydrothermal alteration assemblages ~~(Laureijs et al., 2021)~~(Laureijs et al., 2021a; Laureijs et al., 2021b), magmatic and metamorphic events (Li et al., 2020; Tamblyn et al., 2020), as well as metallogenic systems (Olierook et al., 2020; Redaa et al., 2021b; Şengün et al., 2019) whilst still preserving their micro-scale textural context.

Commented [DS15]: Reviewer 1: Clay minerals present in shales are barely visible with naked eyes, please re-phrase.

Commented [DS16R15]: Done.

Commented [DS17]: Reviewer 1: …the samples analysed and of the fluids involved.

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Another novel use of this technique is to date Proterozoic shales in order to constrain their depositional window (Subarkah et al., 2021). Evidence suggests that clay minerals in Proterozoic shales are dominated by authigenic products from reverse weathering processes during reactions in equilibrium with the ~~water-column~~ formation waters ~~(~~(Deepak et al., 2022; Isson and Planavsky, 2018; Kennedy et al., 2006; Mackenzie and Kump, 1995; Rafiei and

Commented [DS21]: Reviewer 1: 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).

Commented [DS22R21]: Done.

Kennedy, 2019; Rafiei et al., 2020). Conversely, clay assemblages in late Ediacaran and Phanerozoic shales are commonly dominated by detrital products from continental weathering and erosion of soils and unstable parent rocks (Baldermann et al., 2020; Chamley, 1989; Galán, 2006; Hillier, 1995; Kennedy et al., 2006; Rafiei et al., 2020; Singer, 1980; Wilson, 1999). Simple multicellular organisms such as fungi and lichen have been shown to dramatically influence the rate of chemical weathering in continental rocks (Chen et al., 2000; Cuadros, 2017; Kennedy et al., 2006; Lee and Parsons, 1999; McMahon and Davies, 2018; Mergelov et al., 2018; Rafiei et al., 2020). As such, the surge in abundance of detrital clays in shales in the Ediacaran and Phanerozoic has been attributed to the production of soils driven by emergence of these microorganisms (Kennedy et al., 2006; Lee and Parsons, 1999; McMahon and Davies, 2018; Mergelov et al., 2018; Rafiei and Kennedy, 2019; Zambell et al., 2012). Thus, the primarily authigenic nature of clay minerals in Proterozoic shales make them ideal targets for *in situ* Rb–Sr dating (Subarkah et al., 2021).

Despite the promising potential of the Rb–Sr isotopic system, the chronometer still holds some limitations. Rb and Sr are large ion lithophile elements that can sit in well-bound interstitial sites within a mineral lattice as well as adsorbed onto the surface where they are more susceptible to fluid mobilisation (Li et al., 2019; Nebel, 2014; Villa, 1998). In these environments, fluid-induced recrystallisation and alteration can drive element and isotopic exchange at lower effective closure temperatures than those empirically determined for classic thermal volume diffusion reactions (Dodson, 1973; Field and Råheim, 1979; Jenkin et al., 1995; Villa, 1998). Nevertheless, these ~~weaknesses~~complications can in turn be used advantageously to date secondary events such as episodes of hydrothermal fluid-flow (Dodson, 1973; Li et al., 2020; Redaa et al., 2021b; Shepherd and Darbyshire, 1981; Subarkah et al., 2021; Tamblyn et al., 2020). However, it should be noted that the Rb–Sr system in shale-hosted illite may also be affected during diagenesis via the transformation of smectite to illite-smectite mixed layer minerals.

In this study, we ~~show how *in situ* Rb–Sr analysis of the Proterozoic~~dated the Mesoproterozoic Velkerri Formation ~~in~~from the Roper Group~~,~~ of the McArthur Basin~~,~~ in northern Australia ~~(Figure 1) dated~~ by *in situ* Rb–Sr geochronology and show that clay-mineral ~~recrystallisation~~recrystallization in these shales occur at similar temperatures ~~similar~~ to kerogen catagenesis. The Roper Group is a good case study for *in situ* Rb–Sr shale dating, as it has been shown to be dominated by authigenic clays (Rafiei and Kennedy, 2019; Subarkah et al., 2021) and is chronologically well-constrained (Ahmad and Munson, 2013; Bodorkos et al., ~~2020~~2022; Cox et al., 2022; Kendall et al., 2009; Southgate et al., 2000; Subarkah et al., 2021; Yang et al., 2020). Furthermore, the resurgence of ~~energy exploration~~interest in the

Commented [DS23]: Reviewer 1: …and erosion of soils and unstable parent rocks".

Commented [DS24R23]: Done.

Commented [DS25]: Reviewer 1: 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.

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Commented [DS27]: Reviewer 2: The combination of the methods have been shown to provide thermochronological constraints, but since the authors repeatedly emphasize its utility, may it be described what actually makes this particular combination so powerful and how it distinguishes from other thermochronological methodological schemes?

Commented [DS28R27]: Explained here and in the discussions section of the manuscript. Primarily, other thermochron like K-Ar, Ar-Ar, fission tract (zircon, apatite) that date the surrounding sediments and make inferences on if this applies to the shales (or organic-rich units they want to constrain). They are also destructive to the petrographic context of each sample, time consuming, and expensive. On the other hand, traditional temperature constraints in petroleum systems (Tmax, vitrinite/bitumen reflectance, aromatic hydrocarbons) don't provide age data. This method allows for direct dating of these shales, and couple them with the thermal proxies previously mentioned. This is unique, fast and an affordable way to collect considerable useful data.

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Commented [DS30R29]: Done.

resource potential of the organic-rich Velkerri Formation has also yielded a framework of ~~geothermal~~palaeotemperature data that aim to discern the maturation history of hydrocarbons within the unit (Ahmad and Munson, 2013; Capogreco, 2017; Cox et al., 2016; Crick et al., 1988; George and Ahmed, ~~2002~~2002a; Jarrett et al., ~~2019~~2019a; Lemiux, 2011; Revie, 2014; Summons et al., 1994; Taylor et al., 1994; Volk et al., 2005).

Here, we targeted the Velkerri Formation (Figure 1) from the thoroughly investigated well Altree 2 (Capogreco, 2017; Cox et al., 2022; Cox et al., 2016; George and Ahmed, ~~2002~~2002a; Jarrett et al., ~~2019~~2019a; Lemiux, 2011; Nguyen et al., 2019; Nixon et al., 2021; NTGS, 1989, 2009, 2010, 2012; Revie, 2014; Sander et al., 2018; Yang et al., 2018). We show that common hydrocarbon maturation proxies such as T_{max} data from Rock-Eval pyrolysis, aromatic hydrocarbons, bitumen reflectance, and illite crystallinity can help define the temperature sensitivity of the Rb–Sr isotopic system in organic-rich shales. In addition, we have also modelled the geothermal aureole of a mafic intrusion that may have matured the kerogen into the gas window, altered trace elemental signatures and reset the Rb–Sr isotopic system within the unit. As a result, we demonstrate that combining this novel dating method with traditional kerogen maturation proxies ~~is~~can be a powerful tool for reconstructing the thermochronological evolution of Proterozoic basin systems~~ and~~. This approach can then be applied to aid in hydrocarbon exploration ~~in~~for similar settings.

2 Geological Background

The Palaeo-to-Mesoproterozoic greater McArthur Basin is an intra-cratonic sedimentary system exposed across 180,000 km^2 of northern Australia (Ahmad and Munson, 2013). The basin is sub-divided into five unconformity-bounded sedimentary packages characterized by similarities in age, lithology, and stratigraphic position (Jackson et al., 1999; Rawlings, 1999). The Roper Group is part of the Wilton Package which is the youngest of these sub-divisions (Jackson et al., 1999; Jackson et al., 1987; Munson, 2016; Rawlings, 1999). The thickness of the Roper Group varies around 1 to 5 km across several different fault zones (Abbott and Sweet, 2000; Abbott et al., 2001; Ahmad and Munson, 2013; Jackson et al., 1987; Rawlings, 1999). The Beetaloo Sub-basin (Figure 1) is interpreted to be the main depocentre of the sedimentary system and preserves the thickest Roper Group ~~is thickest here~~sequences (Abbott and Sweet, 2000; Ahmad and Munson, 2013; Jackson et al., 1987; Plumb and Wellman, 1987). Lithologically, the Roper Group comprises of a series of coarsening-up sequences dominated by marine mudstone and interbedded sandstone with minor successions of intraclastic limestone (Abbott and Sweet, 2000; ~~Ahmad and Munson, 2013;~~ Jackson et al., 1987; Munson, 2016; Yang et al., 2018). Records of water-column euxinia and redox stratification, as well as fluctuating salinity levels, suggests that the Roper Group formed in an intermittently restricted marine basin within an epicontinental setting similar to the modern Black Sea, or Baltic Sea (Ahmad and Munson, 2013~~; Beyer et al., 2016~~; Cox et al., 2022; Cox et al., 2016; Mukherjee and Large, 2016; Revie and MacDonald, 2017; Yang et al., 2018).

Age constraints of the Roper Group have been established through several geochronological methods (Ahmad and Munson, 2013; Jackson et al., 1999; Kendall et al., 2009; Nixon et al., 2021; Page et al., 2000; Southgate et al., 2000; Subarkah et al., 2021; Yang et al., 2019; Yang et al., 2020; Yang et al., 2018). The beginning of the group's genesis is bracketed by a SHRIMP U–Pb zircon study from a tuff within the unconformably underlying Nathan Group as well as minimum depositional age from an *in situ* Rb–Sr analysis in the lower Roper Group that yielded ages of 1589 ± 3 Ma and 1577 ± 56 Ma, respectively (Page et al., 2000; Subarkah et al., 2021). The unconformity between the Roper Group and the ~~older~~immediately underlying Nathan Group is likely related to the Isan Orogeny ca. 1.58 Ga (Ahmad and Munson, 2013; Jackson et al., 1999). Absolute dating of the Roper Group has been obtained through two SHRIMP U–Pb zircon studies from tuff layers in the Mainoru Formation resulting in ages of 1492 ± 4 Ma and 1493 ± 4 Ma (Jackson et al., 1999; Southgate et al., 2000). On the other hand, the Kyalla Formation at the top of the Roper Group is constrained to being deposited between the U–Pb age of its youngest detrital zircon at 1313 ± 47 Ma (Yang et al., 2018) and the age of ~~the crosscutting Derim Derim dolerite intrusion at 1313 ± 1 Ma (Yang et al., 2020)~~crosscutting Derim Derim dolerite intrusions at 1313 ± 1 Ma, 1324 ± 4 Ma, and 1327.5 ± 0.6 Ma (Bodorkos et al., 2022; Yang et al., 2020).

~~The Velkerri Formation within the Roper Group is the focus of this study and mature~~Mature organic-rich shales from the ~~unit~~Velkerri Formation have been dated by Re–Os analysis at 1417 ± 29 Ma and 1361 ± 21 Ma (Kendall et al., 2009). These ages have been interpreted to be the depositional age of the formation. The geochronological constraints of the Roper Group are summarized in Figure 1. The Velkerri Formation is dominated by deep-basinal lithologies such as ~~black~~ mudstones and ~~silts~~siltstones that coarsens-up into the cross-bedded Moroak Sandstone and Sherwin Ironstone (Abbott et al., 2001). The ~~unit~~Velkerri Formation is interpreted to represent a deep-water, high-stand systems tract within a marine environment (Abbott et al., 2001; Warren et al., 1998). The Velkerri Formation is commonly sub-divided into three distinct ~~Upper, Middle~~members (from bottom to top, the Kalala, Amungee, and ~~Lower~~Wyworrie Members) based on ~~their~~ variations in total organic carbon (TOC) content, gamma ray response,

Commented [DS31]: Reviewer 1: 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,

Commented [DS32R31]: Both comparisons have been previously made in literature as seen in Ahmad and Munson (2013), Yang et al., (2020), and Cox et al., (2022).

Commented [DS33]: Reviewer 1: 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 that the depositional age of the shale, so better say that the Kyalla Formation is somewhat older than 1313 Ma.

Commented [DS34R33]: 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.

Commented [DS35]: Reviewer 1: Depositional age or diagenetic age, given that we look at authigenic clays?

Commented [DS36R35]: This was in relation to the Re-Os age referenced in literature, which has been interpreted as the depositional age. We have rewritten this for clarity.

geochemistry, sedimentology and mineralogy (Ahmad and Munson, 2013; Cox et al., 2016; Cox et al., 2019; Jarrett et al., 2019b; Munson and Revie, 2018; Revie, 2016; Warren et al., 1998).

Importantly, the McArthur Basin experienced a complex thermal history following the deposition of the ~~Wilton Package.~~ Roper Group Mafic sills of the Derim Derim Dolerite widely intrude all units in the Roper Group at ca. 1330~~–1295~~1300 Ma, with the ~~early~~oldest intrusions likely contemporaneous with the end of sedimentation in the basin (Ahmad and Munson, 2013; Bodorkos et al., ~~2020~~2022; Nixon et al., 2021; Subarkah et al., 2021; Yang et al., 2020). Little evidence of subsequent tectono-thermal perturbation is present within the basin until much of the region was overlain by subaerial basaltic lavas of the Kalkarindji Large Igneous Province (LIP) extruded at ca. 510 Ma (Evins et al., 2009; Glass and Phillips, 2006; Jourdan et al., 2014; Nixon et al., 2022)~~. Following the Cambrian expulsion of the Kalkarindji lavas, no significant (> 110°C; Nixon et al., submitted) thermal elevation has been detected within the shallow basin (Duddy et al., 2004)~~. Following the Cambrian eruption of the Kalkarindji lavas, no significant (> 110°C) heating has been detected within the shallow parts of the basin (Duddy et al., 2004; Nixon et al., 2022).

The Altree 2 well drilled in the Beetaloo Sub-basin ~~is~~was chosen for this study as it intersects the entirety of the Velkerri Formation (Figure 2). In addition, ~~it bottoms out in an intrusion of the Derim Derim Dolerite and includes~~the well also intersected lavas of the Kalkarindji LIP ~~that~~ directly ~~overlie~~overlying the Proterozoic sedimentary rocks and terminated at an intrusion of the Derim Derim Dolerite. Importantly, this well has also been the focus of numerous geochronological, geochemical and geobiological investigations from academia, private explorers as well as the Northern Territory Geological Survey (NTGS) which provide important complementary data to supplement this study (Bodorkos et al., ~~2020~~2022; Cox et al., 2022; Cox et al., 2016; Cox et al., 2019; George and Ahmed, ~~2002~~2002a; Jarrett et al., ~~2019~~2019a; Lemiux, 2011; Nguyen et al., 2019; Nixon et al., 2021; NTGS, 2009, 2010, 2012; Sander et al., 2018; Warren et al., 1998; Yang et al., 2018).

3 Methodology

Rock-Eval pyrolysis, aromatic hydrocarbon results, bitumen reflectance values, bulk x-ray diffraction (XRD) mineralogical compositions, and well log data were collated from several sources and compiled together in this study (Capogreco, 2017; Cox et al., 2016; Jarrett et al., 2019b; Lemiux, 2011; NTGS, 1989, 2009, 2010, 2012; Revie, 2014; Revie et al., 2022). As such, their corresponding methodologies can be found in the references therein. The lithology of the Velkerri Formation was interpreted in detail (Figure 2) using the electrical logs Gamma-Ray (GR), Neutron

Commented [DS37]: Reviewer 2: Are there any tectono-thermal perturbation that would be expected to have affected the area, and if so, when and of what type? Any orogeny that may have disturbed radiogenic isotopic system?

Commented [DS38R37]: Recent AFT thermochronology data presented by Nixon et al. (2022) across the McArthur Basin does indicate slow regional cooling during the Devonian-Ordovician Alice Springs Orogeny, attributed to minor regional uplift concurrent with this event. Crucially, there is no observed major structural reactivation within the basin associated with this event. This study does not find evidence for any other thermal perturbation within the basin following the Cambrian. Furthermore, no orogenic reworking is preserved in the McArthur Basin or regional basement in the form of metamorphism, igneous intrusion, large scale folding or angular unconformities, suggesting this region has not experienced major orogenesis following the Proterozoic.

Commented [DS39]: Reviewer 1:
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?

Commented [DS40R39]: 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.

(NRS) and Density (RHOB) of the Altree-2 well (NTGS, 1989). Four lithologies were defined after applying cut-offs at each electrical log. They are then correlated along depth. Sandstone units corresponds to a GR < 130 API, NRS < 0.20 ~~m^3/m^3~~% and RHOB of around 2.5 ~~gr~~g/cm^3. This relates to a cross over between the RHOB and NPRS logs and competent material at the GR. Interbedded shale and sands are defined by a GR > 130 and < 250 API, NRS > 0.20 and < 0.25 m^3/m^3 and RHOB between 2.5 and 2.53 ~~gr~~g/cm^3. This lithology reflected a smaller breach between the density and neutron logs in comparison to the previous sandstone lithology. Shale units were constrained by a GR > 250 API, Neutron > 0.25 m^3/m^3 and RHOB > 2.53 ~~gr~~g/cm^3 and a minimum to no separation between the porosity logs. On the other hand, dolomitic siltstones have a GR response similar to the sandstone, with NRS ranging between 0.25 to 0.27 and RHOB > 2.62 ~~gr~~g/cm^3. This indicates a competent lithology in the GR with a gap between the neutron and density curves. In addition, ~~the~~ T$_{max}$ ~~log and TOC content was also~~data were also collated to discriminate the hydrocarbon maturation levels downhole. From this, a shift in hydrocarbon potential and T$_{max}$ gradients were identified at around 900 m (Figure 2~~).~~), where kerogen enters the gas window and becomes overmature. Five shale chips were then sampled from the Velkerri Formation in Altree 2 at depths of 415 m, 520 m, 696 m, 938 m, and 1220 m for further characterisation.

Samples were first imaged for their mineral composition and petrographic relationships. Back Scatter Electron (BSE) imaging and Mineral Liberation Analysis (MLA) maps of samples were collected using a Hitachi SU3800 Automated Mineralogy Scanning Electron Microscope at Adelaide Microscopy. BSE image tiles were done at 10 mm working distance and 20kV acceleration voltage.~~ with~~ MLA maps were completed using a raster analysis with spectra collected at 0.35 µm/pixel resolution. Minerals previously categorised by bulk XRD analysis of the Velkerri Formation from Cox et al. (2016) were used to develop a 'library' to help identify phases found by spectral reflectance MLA mapping.

In situ Rb–Sr geochronology and trace element analysis were undertaken at Adelaide Microscopy using a laser ablation (RESOlution-LR ArF 193nm excimer laser) inductively coupled plasma tandem mass spectrometer (Agilent 8900x ICP-MS/MS) with the analytical parameters and tuning conditions following Redaa et al. (2021a)~~ and the specific~~. The laser ~~setup can be found~~set-up used in ~~the reference.~~this study is provided in the Supplementary Material. Laser ablation data and error correlations were processed using the LADR software package ~~(Norris and Danyushevsky, 2018) and isochron ages were calculated with ISOPLOTR (Vermeesch, 2018).~~ (Norris and Danyushevsky, 2018; Schmitz and Schoene, 2007). During the data-processing step, Zr, Si, Ti, and rare earth element signatures were monitored to filter the detrital component of each analysis. Non-stable isotopic and elemental

Commented [DS41]: Reviewer 1: Use of the word "sands". Isn`t it sandstone or weakly consolidated sandstone, given that metamorphic rocks (shale) are involved?

Commented [DS42R41]: Done.

Commented [DS43]: Reviewer 1: collated // collected

Commented [DS44R43]: Collated is correct here.

Commented [DS45]: Reviewer 1: were // where

Commented [DS46R45]: Done/

Commented [DS47]: Reviewer 1: at depths of

Commented [DS48R47]: Done.

Commented [DS49]: Reviewer 1:…acceleration voltage. MLA maps were collected

Commented [DS50R49]: Done.

Commented [DS51]: Reviewer 1: Which chemical criteria were chosen to distinguish between smectite, illiite 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.

Commented [DS52R51]: 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.

Commented [DS53]: Reviewer 1: Adelaide Microscopy – is this correct?

Commented [DS54R53]: Yes.

signatures were also culled or cropped during the processing of each analysis to aid in ensuring spot homogeneity. The ^{87}Rb decay constant used was 0.000013972 ± 4.5e-7 Myr^{-1} following Villa et al. (2015). Isochron and single-spot ages were calculated with ISOPLOTR (Vermeesch, 2018). Single-spot ages were calculated using the isochron intercept as their initial ^{87}Sr/^{86}Sr ratios (Nebel, 2014; Rösel and Zack, 2022; Vermeesch, 2018). In addition, kernel density estimation (KDE) graphs (Vermeesch, 2012), cumulative age distributions (CAD) plots (Vermeesch, 2007), and multidimensional scaling (MDS) graphs (Vermeesch, 2013) were also constructed using ISOPLOTR (Vermeesch, 2018) to differentiate between the population of single-spot ages from each sample.

Commented [DS55]: Reviewer 2: Continuing on the illite mixing topic, estimates of the illite homogeneity can also be provided by dissecting isotopic ratios in each LA spot signal in the absence of grain size separation. Please provide a detailed account on how the procedure of analysing spot homogeneity was carried out, on the outcomes and conclusions drawn from the observations, and mention any implications for the age results going from single downspot time frames to the combination of spots in the isochron diagram.

Commented [DS56R55]: During processing, each spot was filtered by filtering bad signals (Si, Zr, not stable signals etc.). We like the idea of investigating single-spot isotopes variations for future investigation, but suggest that this is not required here. We calculated single-spot ages to further confirm that each spot in each sample consisted of clay phases that might not be homogeneous, but still form at the same time. This heterogeneity can actually be a positive, providing a good spread in the isochron and resulting in better errors.

Commented [DS57]: Reviewer 1: Were the Sr initials calculated from the isochrons or assumed to reflect Proterozoic seawater?

Commented [DS58R57]: Calculated from the isochrons.

The ~~phologopite~~phlogopite nano-powder Mica-Mg (Govindaraju et al., 1994) was used as the primary reference material and its natural mineral equivalent MDC from ~~Bekily~~the Ampandrandava Mine in Madagascar (Armistead et al., 2020; Hogmalm et al., 2017; Li et al., 2020; Redaa et al., 2021a) as well as glauconite grain reference material GL-O (Charbit et al., 1998; Derkowski et al., 2009) were used secondary age standards. As previously discussed in Subarkah et al. (2021), nano-powdered reference materials have similar ablation characteristics to fine-grained shales, with analogous matrix effects. As such, they are ideal standards for *in situ* analyses of these samples.

When anchored to a ^{87}Sr/^{86}Sr initial ratio = 0.72607 ± 0.00363 as reported by Hogmalm et al. (2017), MDC yielded an age of 524 ± 7 Ma. This is within error of the published mean age of Mica-Mg at 519 ± 7 Ma (Hogmalm et al., 2017). In addition, the independent reference material GL-O gave an age of 96 ± 4 Ma, accurate to its published K–Ar age of ~~93 ± 4~~95 ± 1.5 Ma (Charbit et al., 1998; Derkowski et al., 2009)~~. Glass standards~~. It should be noted that this age is younger than the tuff-horizon age of the GL-O host rock, dated at 113 ± 0.3 Ma (Selby, 2009). Consequently, the ages yielded from GL-O have instead been proposed to be indicative of the formation of glauconite occurring early after the deposition of the host rock (Selby, 2009).

Commented [DS59]: Reviewer 1: The GLO age should be somewhat older (~100 Ma), because the host rock is of lower Cenomanian age. Please comment on this.

Commented [DS60R59]: 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.

Glass standard NIST SRM 610 was used as a primary standard for elemental quantification in this study. Analysis of secondary standard BCR-2G yielded major, trace and rare earth element composition that were in good agreement (Pearson R > 0.999, Pearson R^2 > 0.999, and P Value < 0.0001) with their published values as compiled in the GeoREM database (Jochum and Stoll, 2008; Jochum et al., 2011; Jochum et al., 2005; Pearce et al., 1997).

One-dimensional thermal modelling of the Altree 2 well was conducted using the SILLi 1.0 numerical model, which is designed for simulating thermal perturbation associated with sill emplacement within sedimentary basins (Iyer et al., 2018). First, palaeotemperatures were estimated from the compiled ~~T_{max}~~thermal maturity data (Disnar, 1986, 1994; Waliczek et al., 2021) following equations based on similar sedimentary systems that experienced a heating event due to burial and a subsequent igneous intrusion (Piedad-Sánchez et al., 2004). Forward modelling was then conducted to replicate maximum thermal conditions ~~predicted~~calculated in the well from ~~T_{max}~~the thermal maturity data, where palaeotemperatures suggest that the ~~Upper~~Wyworrie and ~~Middle Velkerri Formation~~Amungee Members experienced significant additional sedimentary cover ~~present during~~in the Mesoproterozoic. During modelling, an additional 1.5 km of sedimentary rocks were added above the erosional unconformity now present above the McArthur Basin~~,~~ fill (Hall et al., 2021), while all post-Mesoproterozoic units were excluded. The upper contact of a sill with an initial temperature of 1150°C (Wang et al., 2012)) was set at ~~2368~~2868 m, in accordance with adjusted burial depths during the Mesoproterozoic. As sill thickness is unconstrained within the Altree 2 well, multiple iterations were run with different thicknesses in order to establish the scenario able to best satisfy the thermal aureole extent observed in this well. From this, a sill thickness of 75 m was considered most appropriate, and is consistent with Derim Derim sill thicknesses of ~10–100 m commonly observed across the basin (Lanigan and Ledlie, 1990; Lanigan and Torkington, 1991; Ledlie and Maim, 1989; NTGS, 2014, 2015, 2016). Full modelling parameters and ~~geophysical~~petrophysical properties are provided in the Supplementary Material Table S2 and Table S3.

4 Results

4.1 Compilation of legacy data

All legacy data are compiled in the Supplementary Material and were checked for quality before ~~starting~~ interpretation as several factors such as contamination of cuttings due to drilling fluid or poor organic content can make results unreliable (Carvajal-Ortiz and Gentzis, 2015; Dembicki Jr, 2009; Peters, 1986). ~~As such,~~ Rock-Eval pyrolysis values were screened using the thresholds described by Hall et al. (2016). Data were subsequently excluded from interpretation if these criteria were not met. More than 90% of the data yielded S2 > 0.1 mg HC/g, indicating that they were sufficiently abundant in organic content to provide well-defined peaks for characterising T_{max} and Hydrogen Index. Importantly, compilation of Rock-Eval pyrolysis values were all internally consistent (e.g., Hydrogen Index = S2/TOC x 100). Next, there was no evidence of anomalously low T_{max} values (< 380°C) present. Extremely low T_{max} values are commonly a product of incorrect selection of the S2 peak by the program or the widening of the S1 peak from non-indigenous free hydrocarbons. T_{max} results compiled in this study range~~s~~ between 384°C to 502°C with a

Commented [DS61]: Reviewer 1: Is there any mineralogical evidence for the assumed temperature of the sill, such as high-T mineral assemblages?

Commented [DS62R61]: 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).

Commented [DS63]: Reviewer 2: How may any lateral variations in the geological setting and the processes and events affecting the rock sequence impact the conclusions drawn on the timing, spatial occurrence and sheer cause of isotopic disturbance given that conclusions are based on a modelled vertical line?

Commented [DS64R63]: The vast majority of the thermal regime is controlled in the vertical dimension, which in this case is also the dimension in which the best geological constraints are present. Geologically, lateral transfer of heat is minimal, hence the prevalence of 1D models (e.g. Hall et al., 2020). Additionally, modelling in 2D or 3D space would require robust knowledge of the lateral geology which is not available such that it would improve reliability of our models. The only lateral thermal scenario which would significantly impact this model would be the emplacement of a (very) nearby intrusion at modelled stratigraphic levels which would increase temperatures broadly across the vertical sequence. Given there is no evidence for such a proximal intrusion, and thermometers from this well are adequately explained by the currently proposed overburden and bottom-hole intrusion (Figure 7), we suggest the current 1D model is appropriate. Furthermore, no major aquifers have been identified in the Velkerri Formation, suggesting that the potential for lateral fluid flow is unlikely.

Commented [DS65]: Reviewer 1: Tmax results compiled in this study range

Commented [DS66R65]: Done.

mean of 433°C (st. dev. = 17). TOC content in the Velkerri Formation varies from 0.07% to 8.07%, averaging at 2.25% (st. dev. = 2.26).

Clay mineral crystallinity and size data sourced for this compilation were standardised for interlaboratory comparisons (Warr and Mählmann, 2015; Warr and Rice, 1994). Full~~-~~ width at half maximum values from Altree 2 shale samples were computationally remeasured as a secondary check (Capogreco, 2017; NTGS, 2010, 2012). Thirteen samples from the Velkerri Formation were analysed for their illite crystallinity. The Kübler Index for these shales range between 0.88 to 0.36, with decreasing values at depth and the lowest data originating from the ~~Lower Velkerri Formation.~~ Kalala Member. Methylphenanthrene distribution factor (MPDF), methylphenanthrene ratios (MPR), and bitumen reflectance data collated from Jarrett et al. (2019a) and Revie et al. (2022) also displays an increasing trend down-hole.

4.2 Mineralogy of the Velkerri Formation

Eleven mineral phases were identified by bulk XRD analysis of the Velkerri Formation from Cox et al. (2016). The major mineral phases were quartz, kaolinite, illite, and orthoclase, which on average make up 90% of the total composition of the samples. Trace minerals include glauconite, montmorillonite, pyrite, magnetite, siderite, dolomite, and plagioclase. Our MLA mapping~~ in this study~~ also identified these assemblages. Importantly, the two different methods categorised these minerals at similar abundances. However, results from MLA mapping also found other mineral assemblages not identified by bulk XRD analysis~~. This includes~~, including biotite, chlorite, clinochlore, apatite, and zircon. These differences could be due to the slightly different sub-intervals from which samples were analysed. Bulk XRD is a destructive procedure and therefore, the same section cannot be reused for *in situ* analysis. ~~As a result, samples might slightly differ 1 – 2 cm apart.~~As a result, samples spaced 1 – 2 cm apart may yield different results. In addition, the targeted areas for MLA are often spatially localised and only based on 2D information. As such, they may not be representative for the bulk rock, making the comparison with XRD datasets difficult. The complete mineralogical abundance and correlations between results bulk XRD and MLA mapping are summarised in Table 1. Extensive petrographic descriptions of all samples can be found in the Supplementary Material.

4.3 Laser ablation data

Geochronological results yielded by samples from the ~~Upper~~Wyworrie and ~~Middle Velkerri Formation~~Amungee Members gave ages within error of each other. The sample from 415 m depth was dated at ~~1470 ± 102~~1448 ± 81 Ma.

Commented [DS67]: Reviewer 1: Can provide XRD patterns of illite and clay assemblages) to prove the absence of interstratified I-S in their samples?

Commented [DS68R67]: Done.

Commented [DS69]: Reviewer 1: 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.

Commented [DS70R69]: XRD patterns now provided in the Supplementary Material.

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Commented [DS71]: Reviewer 1: 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). Clinochlore is a Mg-rich chlorite – what is the difference between chlorite and clinochlore here?

Commented [DS72R71]: Some clay phases have been identified as products of alteration of detrital feldspar. This is now discussed in the Supplementary Material. The SEM instrument used here has differentiated between chlorite and clinochlore. Chlorite and clinochlore is now combined clarity.

Commented [DS73]: Reviewer 1: 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.

Commented [DS74R73]: 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.

Commented [DS75]: Reviewer 1: 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.

Commented [DS76R75]: Done.

Commented [DS77]: Reviewer 1: bulk XRD and MLA mapping results are summarized…

Commented [DS78R77]: Done.

Next, the mudstone analysed from 520 m depth yielded an age of ~~1457 ± 29~~1434 ± 19 Ma. Thirdly, the shale sample studied from 696 m depth resulted in an age of ~~1421 ± 152~~1411 ± 139 Ma. A ~~Lower Velkeri Formation~~Kalala Member shale chip from 938 m at depth was dated at ~~1318 ± 105~~1322 ± 93 Ma. Another sample from this member, towards the boundary ~~into~~with the underlying Bessie Creek Sandstone at depth 1220 m resulted in an age of ~~1332 ± 67~~1336 ± 40 Ma. The range of precision from these Rb–Sr ages are primarily constrained by a ~~good~~substantial spread in ^{87}Rb/^{86}Sr ratios, the number of data points defining the regression line as well as errors on each individual analysis (Nebel, 2014). The most precisely dated samples, extracted from 520 m and 1220 m depth, had the widest range of ^{87}Rb/^{86}Sr ratios (0 – 50) whilst the other two samples preserved a range of ^{87}Rb/^{86}Sr values less than 10 (Figure 6). The variability in these values could be a subject of future studies in order to improve the success of this dating method. Single-spot ages were calculated for all spot analyses in each sample, and their populations categorically differ (Figure 8).

Commented [DS79]: Reviewer 1: Why is the age uncertainty so high in case of the shale samples investigated?

Commented [DS80R79]: This is discussed in the end of this paragraph. Some samples simply do not have a wide range in Rb/Sr ratios, or are not abundant in Rb.

Elemental concentrations of each sample were concurrently collected during the *in situ* Rb–Sr laser ablation investigation and they are in good agreement with data collected by bulk geochemical analysis from Cox et al. (2016). Samples from depth 415 m, 520 m, and 696 m do not show any covariation between their total REEY concentrations and Sm/Nd ratios (Figure 7). On the other hand, sample 938 m showed a statistically significant relationship between these two parameters (Pearson R = 0.58, Pearson $R^2 = 0.336$, P Value < 0.0001). In addition, Velkerri Formation shale sourced from depth 1220 m also showed a strong covariation between total REEY values and Sm/Nd (Pearson R = -0.545, Pearson $R^2 = 0.297$, P Value < 0.0001). These associations were also identified in the whole-rock geochemical data collected from Cox et al. (2016). Figure 7B ~~showed~~shows that samples between 390 – 900 m depth hold no statistically significant relationships between the two factors. However, samples from deeper than 900 m display a strong relationship between the two variables (Pearson R = -0.559, Pearson $R^2 = 0.312$, P Value = 0.003). The full geochronological and inorganic geochemical dataset for samples in this study can be found in the Supplementary Material.

4.4 Thermal Modelling

One-dimensional thermal modelling of the emplacement of a 75 m thick Derim Derim Dolerite sill at the base of the Altree 2 well is sufficient to produce a thermal aureole reaching temperatures > ~~100~~110°C, ca. 800 m ~~from~~above the top contact of the sill ~~top~~ (Figure ~~8A~~9A). Maximum palaeotemperatures recorded in the ~~upper Velkerri Formation~~Wyworrie Members exceed those predicted in this simulation, however, this may be attributed to elevated temperatures in the shallow basin during eruption of the Kalkarindji LIP in the Cambrian ~~(Nixon et al., submitted).~~(Nixon et al., 2022). The resultant maximum thermal profile is consistent with T_{max} derived palaeotemperature estimates and is thus considered a plausible model for the observed data from the well. Post-intrusion temperatures at depths that match the samples with reset Rb–Sr ages are much lower than observed in comparable isotopic systems for thermally induced diffusion (Dodson, 1973; Tillberg et al., 2020; Torgersen et al., 2015; Yoder and Eugster, 1955), with the shallowest reset sample peaking at ca. ~~110~~120°C. Furthermore, elevated temperatures predicted by the modelling are geologically short lived, with temperatures returning to steady-state conditions by approximately half a million years following sill intrusion (Figure ~~8B).~~

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-	~~**Depth: 415 m**~~		~~**Depth: 520 m**~~		~~**Depth: 696 m**~~		~~**Depth: 938 m**~~		~~**Depth: 1220 m**~~	
~~**Mineral**~~	~~Bulk XRD (wt. %)~~	~~MLA Map (wt. %)~~	~~Bulk XRD (wt. %)~~	~~MLA Map (wt. %)~~	~~Bulk XRD (wt. %)~~	~~MLA Map (wt. %)~~	~~Bulk XRD (wt. %)~~	~~MLA Map (wt. %)~~	~~Bulk XRD (wt. %)~~	~~MLA Map (wt. %)~~
~~Apatite~~	~~*0*~~	~~*0*~~	~~*0*~~	~~*0*~~	~~*0*~~	~~*0.31*~~	~~*0*~~	~~*1.2*~~	~~*0*~~	~~*0*~~
~~Biotite~~	~~*0*~~	~~*1.22*~~	~~*0*~~	~~*0.07*~~	~~*0*~~	~~*0.93*~~	~~*0*~~	~~*0*~~	~~*0*~~	~~*0.01*~~
~~Chlorite~~	~~*0*~~	~~*1.32*~~	~~*0*~~	~~*0*~~	~~*0*~~	~~*0*~~	~~*0*~~	~~*0*~~	~~*0*~~	~~*0*~~
~~Clinochlore~~	~~*0*~~	~~*0.01*~~	~~*0*~~	~~*0.08*~~	~~*0*~~	~~*0.06*~~	~~*0*~~	~~*0.06*~~	~~*0*~~	~~*0.01*~~
~~Dolomite~~	~~*0.25*~~	~~*0*~~	~~*0.37*~~	~~*0*~~	~~*0.21*~~	~~*0*~~	~~*0.53*~~	~~*0*~~	~~*0.43*~~	~~*0.05*~~
~~Glauconite~~	~~*0.82*~~	~~*0*~~	~~*2.35*~~	~~*0*~~	~~*1.53*~~	~~*0*~~	~~*1.36*~~	~~*0*~~	~~*1.04*~~	~~*0*~~
~~Illite~~	~~*34.05*~~	~~*35.52*~~	~~*43.28*~~	~~*36.51*~~	~~*27.59*~~	~~*18.48*~~	~~*27.03*~~	~~*22.13*~~	~~*39.36*~~	~~*38.18*~~
~~Kaolinite~~	~~*21.25*~~	~~*7.45*~~	~~*17.14*~~	~~*7.11*~~	~~*2.07*~~	~~*0.00*~~	~~*6.99*~~	~~*5.46*~~	~~*13.99*~~	~~*20.21*~~
~~Magnetite~~	~~*0.36*~~	~~*0.89*~~	~~*0.38*~~	~~*0.00*~~	~~*0.00*~~	~~*0.00*~~	~~*0.33*~~	~~*0.00*~~	~~*0.42*~~	~~*0.00*~~
~~Montmorillonite~~	~~*1.79*~~	~~*9.05*~~	~~*2.01*~~	~~*0.04*~~	~~*1.49*~~	~~*4.00*~~	~~*1.16*~~	~~*0.00*~~	~~*1.66*~~	~~*0.00*~~
~~Orthoclase~~	~~*13.33*~~	~~*11.48*~~	~~*10.01*~~	~~*4.08*~~	~~*13.40*~~	~~*8.27*~~	~~*11.32*~~	~~*3.37*~~	~~*7.32*~~	~~*4.45*~~

9B).

Method	**Apatite**	**Biotite**	**Chlorite**	**Dolomite**	**Glauconite** ~~**Zircon**~~	**Illite**	**Kaolinite**	~~Siderite~~ **Magnetite**	**Montmorillonite**	**Orthoclase**	**Pyrite**	**Quartz**	**Siderite**	**Zircon** ~~Pyrite~~	**Plagioclase**
Bulk XRD	0.00	0.00	0.00	0.25	0.~~00~~82	34.05	21.25	~~1.76~~0.36	1.79	13.33	0.28	26.13	1.76	0.~~28~~00	0.00
MLA Map	0.00	1.22	1.33	0.00	0.~~02~~00	35.52	7.45	0.~~00~~89	9.05	11.48	0.40	23.93	0.00	0.~~40~~02	4.39
Bulk XRD	0.00	0.00	0.00	0.37	~~0.00~~2.35	43.28	17.14	0.~~05~~38	2.01	10.01	0.74	23.67	0.05	0.~~74~~00	0.00
MLA Map	0.00	0.07	0.08	0.00	0.00	36.51	7.11	0.00	0.04	4.08	0.24	47.94	0.00	0.~~24~~00	0.85
Bulk XRD	0.00	0.00	0.00	0.21	~~0.00~~1.53	27.59	2.07	0.00	1.49	13.40	4.11	45.02	0.00	~~4.11~~0.00	4.57
MLA Map	0.31	0.93	0.06	0.00	0.00	18.48	0.00	0.00	4.00	8.27	4.47	60.88	0.00	~~4.47~~0.00	1.41
Bulk XRD	0.00	0.00	0.00	0.53	~~0.00~~1.36	27.03	6.99	0.~~01~~33	1.16	11.32	1.49	43.28	0.01	~~1.49~~0.00	6.50
MLA Map	1.2	0.00	0.06	0.00	0.00	22.13	5.46	0.00	0.00	3.37	1.60	57.79	0.00	~~1.60~~0.00	6.90
Bulk XRD	0.00	0.00	0.00	0.43	~~0.00~~1.04	39.36	13.99	0.~~10~~42	1.66	7.32	0.26	33.56	0.10	0.~~26~~00	1.86
MLA Map	0.00	0.01	0.01	0.05	0.~~01~~00	38.18	20.21	0.00	0.00	4.45	0.01	35.25	0.00	0.01	1.63

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Depth	415 m	520 m	696 m	938 m	1220 m

Depth (m)	Pearson R	Pearson R 95% C.I.	Pearson R^2	P Value
415	*0.922*	*0.784–0.973*	*0.850*	*< 0.0001*
520	*0.866*	*0.648–0.953*	*0.750*	*<0.0001*
696	*0.953*	*0.868–0.984*	*0.910*	*<0.0001*
938	*0.965*	*0.898–0.988*	*0.930*	*<0.0001*
1220	*0.989*	*0.969–0.996*	*0.979*	*<0.0001*

Table 1A. Mineralogical abundance of the Velkerri Formation shales collected by bulk XRD analysis from Cox et al. (2016) and spectral reflectance MLA mapping in this study. ~~B.~~All values are in weight percent. B. Covariation between the mineral phases categorised by both methods.

5 Thermal Maturity of the Velkerri Formation

Geochemical and mineralogical-based thermal maturity indicators collected via Rock-Eval studies and bulk XRD analyses were compiled in this study ~~for~~in order to establish a vertical profile of the Velkerri Formation ~~to~~and assess the local palaeo-thermal structure. The T_{max} parameter, is the temperature at which the maximum rate of hydrocarbon generation occurs during pyrolysis analysis and is a common method used to reconstruct thermal histories of basin systems (Espitalié, 1986; Espitalié et al., 1977; Peters and Cassa, 1994; Welte and Tissot, 1984). Additionally, the Kübler index (KI) is determined by ~~a sample's first X-ray diffraction~~ the 001-reflection ~~peak~~of illite and is also a popular maturation proxy used to classify low-grade metamorphism in pelitic rocks (Blenkinsop, 1988; Guggenheim et al., 2002; Kubler, 1967). However, both of these thermal indicators can be influenced by ~~several~~multiple factors other than burial-related heating and therefore struggle to resolve absolute quantitative palaeotemperatures. ~~Abundance~~Changes in heating rate, abundance in hydrogen, sulphur, and uranium content or the organic richness of samples can result in inaccurate T_{max} values (Dembicki Jr, 2009; Espitalié et al., 1977; Peters, 1986; Yang and Horsfield, 2020). Similarly, the KI has also been shown to be sensitive to several parameters such as changes heating rate and geochemical variability in the sample's initial mineralogy (Abad and Nieto, 2007; Eberl and Velde, 1989; Mählmann et al., 2012; Warr and Mählmann, 2015). In addition, variations in procedures between ~~in laboratory proceedings~~laboratories can further complicate the direct comparison of these values (Cornford et al., 1998; Jarvie, 1991; Peters and Cassa, 1994; Tissot et al., 1987). Consequently, these thermal indicators need to be ~~approached~~treated with caution when applied independently and are more suitable as qualitative discriminators as opposed to absolute

Commented [DS81]: Reviewer 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. Clinochlore is the Mg member of the chlorite family.

Commented [DS82R81]: As previously discussed, the sample analysed in this study will be 1-2 cm apart from the corresponding sample analysed for Bulk XRD. In addition, we also chose samples that were the most fine-grained to minimise detrital input. Therefore, different bedding layers will have a strong control in the abundance of minerals identified. For example, coarser beds will be more abundant in quartz.

Commented [DS83]: Reviewer 1:
Can provide vitrinite reflectance data for a direct temperature assessment?

Commented [DS84R83]: 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.

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Commented [DS85]: Reviewer 1: Kübler index (KI) is determined by the 001-reflection of illite ….

Commented [DS86R85]: Done.

Commented [DS87]: Reviewer 1: Vitrinite reflectance data can provide absolute formation temperatures.

Commented [DS88R87]: As previously discussed, vitrinite is not present in the rock record during the Proterozoic. However, we have calculated vitrinite reflectance equivalents based on several maturity indicators such as Tmax, bitumen reflectance and aromatic hydrocarbon data in this iteration of the manuscript.

Commented [DS89]: Reviewer 1: such as changes in heating rate

Commented [DS90R89]: Done.

Commented [DS91]: Reviewer 1: …or possibly due to the presence of I-S in the samples? Provide XRD patterns for confirmation.

Commented [DS92R91]: XRD patterns now provided in the Supplementary Material.

quantitative parameters. However, such proxies can be more confidently used to estimate palaeotemperatures in sedimentary successions if they show a strong relationship with each other (Burtner and Warner, 1986; Dellisanti et al., 2010; Ola et al., 2018; Velde and Espitalié, 1989; Waliczek et al., 2021). Ultimately, both organic and inorganic indicators are essential for a robust understanding of ~~how~~the thermal histories of sedimentary ~~systems thermally mature~~sequences through time.

In this study, we examine the covariation between the T_{max} values and KI to reconstruct the thermal history of the Velkerri Formation in the Altree 2 well (Figure 3). In our compilation, samples with immature kerogen ($T_{max} < 435$°C) correspond to rocks in the diagenetic zone (KI > 0.45°Δ2θ). This relationship is true in similar studies and generally translates to palaeotemperatures of ca. 100°C (Abad and Nieto, 2007; Dellisanti et al., 2010; Espitalié et al., 1977; Kosakowski et al., 1999; Kubler, 1967).

Interestingly, the samples within the mature oil window (435°C < T_{max} < 465°C) show a wide range of KI values between 0.39 and 0.65°Δ2θ (Figure 3). This is possibly due to the delay between thermal reactions in clay minerals as opposed to organic matter (Ola et al., 2018). Although the maturation of organic matter and the morphology of clay minerals both largely depend on temperature, other processes such as the kinetics of the thermal reaction and geochemical composition of the sample can make these relationships non-linear (Meunier et al., 2004; Ola et al., 2018; Pollastro, 1993; Varajao and Meunier, 1995; Velde and Vasseur, 1992). The disparity between kerogen evolution and the equilibrium stage of illitisation at these temperatures may also play a role in this variability (Dellisanti et al., 2010). Nevertheless, an increase in T_{max} pyrolysis results from these samples still appears to correlate with a decrease in KI values. These thermometers would approximately equate to palaeotemperatures between 100 and 150°C (Árkai et al., 2002; Frey and Merriman, 1999; Kosakowski et al., 1999; Welte and Tissot, 1984).

~~Lastly~~On the other hand, the sample displaying over-mature kerogen (T_{max} > 465°C) ~~understandably~~ corresponds to the smallest KI value (Figure 3) of 0.36°Δ2θ (Dellisanti et al., 2010). These values commonly define the gas window and the anchizone, ~~reaching~~corresponding to palaeotemperatures of ca. 200°C (Árkai et al., 2002; Dellisanti et al., 2010; Kosakowski et al., 1999). Overall, a trend between increasing T_{max} and decreasing KI values (Figure 3) confirms the feasibility of these parameters as thermal maturation proxies (Dellisanti et al., 2010).

~~These thermal parameters can be further examined by inspecting the changes in kerogen type collected by Rock-Eval pyrolysis analysis (Dellisanti et al., 2010; Espitalié et al., 1985; Espitalié et al., 1977). This can be defined by relationships between the hydrogen index (HI), oxygen index (OI), hydrocarbon potential, and TOC content~~ Lastly, the thermal parameters for the Velkerri Formation can be further examined by inspecting the changes in MPDF (Boreham et al., 1988; Kvalheim et al., 1987), MPR (~~Banerjee~~Radke et al., ~~1998; Cooles~~1982; Wilhelms et al., ~~1986; Espitalié et al., 1985; Espitalié et al., 1977; Peters, 1986~~1998)~~. As previously mentioned,~~ ~~T_{max}~~ ~~values down-hole suggests that the organic matter within the Upper and Middle Velkerri formation (depth 390 – 900 m) was within the oil window, reflecting an immature-to-mature source rock (Figure 2). However, there is a notable shift into the gas window occurring at ca. 900 m depth in the Lower Velkerri Formation (Cox et al., 2016; Lemiux, 2011; NTGS, 1989, 2009, 2010, 2012; Revie, 2014). This down-hole shift is mirrored by other Rock-Eval data used to determine kerogen types in the Velkerri Formation (Figure 4). Figure 4 shows that the Upper and Middle Velkerri Formation are dominated by immature-to-mature source rocks with oil prone Type II-III kerogen, suggesting a palaeotemperature window of less than 150°C (Banerjee et al., 1998; Espitalié et al., 1985; Hunt, 1995; Welte and Tissot, 1984). Meanwhile, the Lower Velkerri Formation comprises of source rocks in the over-mature zone with gas-prone Type III kerogen. A subset of samples from the Lower Velkerri Formation plot in the dry gas window, suggesting that they may have reached palaeotemperatures of over 200°C~~ , and bitumen reflectance (Riediger, 1993). Previous studies have shown that aromatic hydrocarbons were effective in providing thermal constraints for the Velkerri Formation (George and Ahmed, 2002b; Jarrett et al., 2019a). These proxies were similarly sensitive to maturity variations from thermally immature to late oil window. As such, we normalise the thermal indicators used in this study by converting them all ~~(Dellisanti et al., 2010; Frey and Merriman, 1999; Hunt, 1995; Welte and Tissot, 1984)~~(Jarrett et al., 2019a; Jarvie et al., 2001; Revie et al., 2022)~~.~~

to calculated vitrinite reflectance values (VR_{CALC}; Figure 4). The VR_{CALC} from four different thermal indicators show that the Velkerri Formation quickly elevated in maturity and enters the gas window at ca. 900 m depths (Figure 4). The agreement of all proxies add further confidence in the temperature constrains used in this study.

Multiple geochemical and mineralogical thermal parameters from our compiled data~~–~~-set demonstrate ~~good covariation~~strong correlation between them, suggesting that the proxies used in this study primarily recorded changes in palaeotemperature as opposed to other possible variables. Notably, ~~three~~five different, independent, source-rock maturation proxies statistically agree ~~with each other~~ and recorded similar ~~temperature intervals.~~step-wise increase in thermal history down-hole. As such, we investigated five samples approaching the geothermal anomaly in the ~~Lower Velkerri Formation~~Kalala Member for *in situ* Rb–Sr and trace element analysis. The changes in thermal maturation indexes throughout the well are used to help constrain the parameters of the Rb–Sr isotopic system in Proterozoic shales.

6 Thermochronological History of the Velkerri Formation

Although some of the geochronological results of these samples may overlap due to their errors (Figure 6), they are still categorically different down-hole (Figure 8). We display these differences by plotting the population of single-spot ages from each sample against each other. Kernel Distribution Estimate (KDE) plots of these results show that the distribution of single-spot ages from samples shallower than 900 m largely overlaps with the Re–Os age constraint (Figure 8A; light pink) for the Velkerri Formation (Kendall et al., 2009). On the other hand, the population of single-spot ages from shales deeper than 900 m instead agree with the age for the Derim Derim Dolerite (Figure 8A; dark pink) intrusion ca. 1330–1300 Ma (Ahmad and Munson, 2013; Bodorkos et al., 2022; Nixon et al., 2021; Yang et al., 2020).

Importantly, these sample-sets are statistically different from each other. This is graphically shown by their cumulative age distribution (CAD, Figure 8B) and Multidimensional Scaling (MDS, Figure 8C) plots. The second of these techniques statistically measures the dissimilarity between different age distributions through the Kolmogorov-Smirnov test (Vermeesch, 2013). In short, similar age distributions will plot closely to each other whilst distributions that are increasingly dissimilar will plot further away (Vermeesch, 2012, 2013). Figure 8B and 8C show that samples shallower than 900 m had age distributions that are similar to each other (Figure 8). Overall, these ages are statistically similar to the Re–Os constraint of the Velkerri Formation (Kendall et al., 2009), suggesting that they likely represent an early diagenetic/burial age soon after deposition. On the other hand, the single-age distributions of samples deeper than 900 m are statistically different to the previous sample set. They form their own cluster, which in turn coincides with the age of the Derim Derim Dolerites (Ahmad and Munson, 2013; Bodorkos et al., 2022; Nixon et al., 2021; Yang et al., 2020). Consequently, the Rb–Sr shales ages from this section are unlikely to date the deposition of the Velkerri Formation, but instead reflect a late-stage hydrothermal resetting induced by the intrusion.

Commented [DS93]: Reviewer 2: The in situ Rb-Sr dating sample set consists of five samples over a ca. 800m depth interval. Given the discrepancy of several hundreds of meters (most shallow effect from the sill is interpreted at 600m or 800m) in the different thermal modelling predictions, please comment on how the sample interval larger than 200m below
696m depth affects the interpretation and uncertainty of the results regarding potential isotopic disturbance of fluid migration.

Commented [DS94R93]: Four different thermal indicators (Tmax, two different aromatic hydrocarbons, bitumen reflectance, see Jarret et al., 2019) suggest that the elevated thermal gradient occurs past 900 m depths. Although the sub-sample set for the Rb-Sr analyses are sparse, the thermal data sample set are more continuous. Based on this and our thermal modelling, the isotopic disturbance should not occur prior to this depth.

Commented [DS95]: Could provide in-situ Rb-Sr glauconite ages (arguably the earliest diagenetic product) and compare with burial diagenetic illite formation ages?

Commented [DS96R95]: 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.

Commented [DS97]: Reviewer 2: The initial Sr values are not anchored to actual data but rather inferred from the isochrones and comes with large error ranges. Since the importance of initial Sr values for tracing crustal fluids and their sources is indeed stated in the manuscript, have any previous data source been considered for narrowing down on them in the stratigraphic sequence, or may new data collection on this be advisable? Given the spread in initial Sr values and their inference from large-error and low-Rb isochrons, it should be explicitly stated that the isochrons produce age errors ranging up to 300 Ma. Many of them overlap each other and several other dating results in the area, and yet their interpretation and meaning is provided without any note or disclaimer. The age errors and their implications for the conclusions based on the dating should be discussed. In addition, the concluding reasoning of the method as a ...

Commented [DS98R97]: Good initial Sr values are limited to the availability of K(Rb)-deficient and Sr-bearing phases (e.g. carbonates) that form concurrently with the illite phases. Sometimes this is simply not available. Ideally, Sr data can be obtained from interbedded carbonates where possible. However, we haven't used the Sr initials from this study to make any interpretations. We also suggest ...

The petrographic characteristics of assemblages in these samples are further evidence that the shales in the Velkerri Formation recorded two distinct thermochronological events. The abundant clays in samples from depth 415 m, 520 m, and 696 m are predominantly illite, with trace amounts of chlorite, kaolinite, and montmorillonite (Table 1). ~~Notably~~However, they do not show typical irregular, angular detrital morphologies (Figure 5, Figure S2A-C). Instead, clay minerals in these samples form a matrix cement, filling in porous spaces, wrapping around detrital grains and suggesting that they formed within the sediment during burial diagenesis (Rafiei and Kennedy, 2019; Rafiei et al., 2020; Subarkah et al., 2021)~~. A minor component of illite can also be seen replacing micas and feldspars.~~. Primary sedimentary structures such compaction of clays along the bedding plane can also still be identified in these samples (Figure 5, Figure S2A-C and Supplementary Material). These petrographic relationships are further discussed in the Supplementary Material and were similarly found in Roper Group shales elsewhere, indicating an early-diagenetic origin (Rafiei and Kennedy, 2019; Subarkah et al., 2021). ~~Importantly~~Moreover, the ages from these samples are all in agreement with the deposition of the Velkerri Formation dated at 1417 ± 29 Ma by Re–Os geochronology (Kendall et al., 2009), suggesting that the ~~analysed bulk composition~~ majority of illite ~~matrix of these samples~~ formed ~~not long~~relatively soon after sediment deposition.

Nevertheless, we also ~~looked~~sought to identify any potential secondary alteration of these shales by analysing their geochemical signatures. Sm/Nd ratios are common geochemical proxies for screening alteration in shales as Nd is preferentially lost relative to Sm during post-depositional processes (Awwiller and Mack, 1989; Awwiller and Mack, 1991). In addition, fluid-rock reactions also have a significant impact on rare earth element and yttrium solubility and transportation during hydrothermal events (Lev et al., 1999; Williams-Jones et al., 2012). Therefore, these parameters can be an effective tool for highlighting fingerprints of post-depositional geochemical mobilisation (Figure 7).

Samples from depths ~~above~~shallower than 900 m show no significant relationships between their total rare earth elements and yttrium (REEY) concentrations and Sm/Nd ratios collected by laser ablation analysis or through traditional bulk trace element geochemistry (Cox et al., 2016). ~~As such, the ages produced by~~ These support an interpretation that these ~~samples can be interpreted as~~ages form a minimum depositional age for the unit ~~and recorded,~~ recording an early diagenetic event as opposed to a late-stage secondary overprint. Furthermore, ~~T_{max} values~~temperature constrains for the Velkerri Formation at depths 390 – 900 m ~~were ca. 435°C, suggesting~~ suggest that they are well-within the oil window (Figure ~~2). In addition, other pyrolysis parameters indicate that samples from~~

Commented [DS99]: Reviewer 2: the illite crystal textures and intermineralic textural relationships are qualitatively described without detailed petrographic images or accounts on variations within samples. Can such be added for the specific samples in this study and compared to previous studies describing these features at the site?

Commented [DS100R99]: Similar point to previous comment again, we have provided more zoomed-in images (Figure 5 and Supplementary Material) and elaborate on petrographic content. And also provided additional comments and comparisons of this to Rafiei et al. (2019) and Subarkah et al., (2021) who worked on high-resolution petrography of Roper Group shales elsewhere.

Commented [DS101]: Reviewer 2: How can such a specific statement be motivated considering the large age errors?

Commented [DS102R101]: We have now shown that the data are distinguishable despite the large errors.

Commented [DS103]: Reviewer 1: formed within the host sediment during burial diagenesis

Commented [DS104R103]: Done.

Commented [DS105]: Reviewer 1: Unclear meaning of “more crystalline morphologies”, re-phrase

Commented [DS106R105]: Done.

~~this subset are dominated by oil-prone Type II kerogen (Figure~~ 3 and 4). As a result, we propose that ~~the geothermal activity that would have driven the hydrocarbons into such parameters are~~this temperature window is not sufficient to disturb the Rb–Sr and trace element systems in these shales.

Conversely, shales collected from depths >~~–~~900 m showed petrographic evidence of post-depositional alteration (Figure 5 and ~~Supplementary Material).~~Figure S2D-E). Clay minerals ~~in~~the 938 m sample ~~from 938 m depth~~ are fissile and foliated~~.~~ (Figure 5). In addition, pyrite and apatite can be observed overgrowing illite and chlorite. Moreover, ~~Lower Velkerri Formation~~illite grains from the Kalala Member shale ~~from~~at 1220 m depth are notably ~~display more~~larger and crystalline ~~morphologies~~ (Figure 5~~). Illite aggregates in this sample preserve~~ and Figure S2D-E), with features inconsistent with an early diagenetic origin~~. They interlock~~ (and Figure S2D-E). Clay minerals were also found interlocking with quartz overgrowth and appear to replace earlier ~~clay matrices. Samples from these depths gave younger ages than those from the subset stratigraphically above them (Figure 6). However, not only are these ages younger than the results from the subset of samples above, they are also younger than the proposed deposition intervals acquired through the Re–Os dating of the unit (Kendall et al., 2009). Instead, these ages are consistent with the emplacement of the mafic Derim Derim Dolerite intersected at the base of the Altree 2 well at depth 1696 m. This intrusion has been dated twice, at 1313 ± 1 Ma and 1328 ± 24 Ma (Nixon et al., 2021; Yang et al., 2020). Consequently, the shale samples from depth below 900 m may have recorded a secondary event induced by the Derim Derim Dolerite.~~assemblages (Figure 5 and Figure S2D-E).

Commented [DS107]: Reviewer 1: Unclear meaning of "more crystalline morphologies", re-phrase

Commented [DS108R107]: Done.

In addition to petrographic and geochronological disparities, samples from depths below 900 m display statistically significant relationships between total REEY concentrations and Sm/Nd ratios (Figure 7). The shale chip analysed from 938 m had a positive relationship between an increase in Sm/Nd ratio and total REEY concentration (Pearson r: 0.580, R-squared: 0.336), while the sample collected from depth 1220 m preserved a negative relationship between Sm/Nd ratio and total REEY values (Pearson r: -0.545, R-squared: 0.297). These associations are similarly reflected in the bulk ~~geochemical~~trace element data collated from Cox et al. (2016). In the compiled data, shales from deeper than 900 m demonstrate a strong affinity between these controls (Pearson r: -0.559, R-squared: 0.312~~), whereas samples above 900 m show no variation (Figure 7B).~~). These alteration indicators are further evidence that the ~~Lower Velkerri Formation~~Kalala Member at depths below 900 m experienced a late-stage secondary heating event~~. This event may have a hydrothermal component~~, as trace ~~and rare earth elemental systems~~elements are more readily mobilised in ~~fluid systems~~hydrothermal reactions (Awwiller and Mack, 1989; Awwiller and Mack, 1991; Condie, 1991; Lev et al., 1999; Poitrasson et al., 1995; Williams-Jones et al., 2012).

Importantly, ~~Rock-Eval pyrolysis data~~thermal indicators from this interval suggest that kerogen in these shales ~~were~~are thermally ~~over mature~~overmature (Figure ~~2)~~3 and ~~are dominated by gas-prone Type III source rocks.~~4). Previous studies have shown that the source rocks in the Velkerri Formation ~~were~~became overmature only when affected by~~ similar~~ magmatic events ~~(Crick et al., 1988; George and Ahmed, 2002). As such, the Derim Derim Dolerite intrusion may have prompted a hydrothermal alteration footprint onto its surrounding sediments. This magmatic pulse would have recrystallised the minerals, disturbed the Rb–Sr chronometer, mobilised trace elements, and heated the hydrocarbons within the Lower Velkerri Formation to overmaturity.~~ (Crick et al., 1988; George and Ahmed, 2002a). As such, it is plausible that the Derim Derim Dolerite intersected in this well has imposed a hydrothermal alteration footprint onto the surrounding sediments via conductive heat loss and/or heat-transfer fluids. This magmatic pulse would have recrystallised the former mineral assemblages or induced a second mineralisation of clays, mobilised trace elements, and heated the kerogen within the Kalala Member to overmaturity. Thermal indicators (Figure 4 and 9) suggest that source-rocks within this interval may have experienced palaeotemperatures of at least 150 °C (Dellisanti et al., 2010; Frey and Merriman, 1999; Hunt, 1995; Welte and Tissot, 1984). This is in good agreement with evidence from aqueous fluid inclusions in quartz veins within the Derim Derim Dolerite elsewhere, which have suggested that hydrocarbons from the Velkerri Formation migrated in the cooling sill at similar temperatures (Dutkiewicz et al., 2004). Importantly, such hydrothermal systems seem to be sufficient for disturbing the Rb–Sr isotopic system of these samples.

~~Overall, the Upper and Middle Velkerri Formation preserve an early diagenetic event not long after deposition of the unit. Petrographic relationships deduced through high resolution spectral reflectance imaging showed that clay minerals in these shales formed cements and grew in pore spaces, replacing micas and feldspars (Figure 5 and Supplementary Material). Furthermore, different geochemical indicators collected by laser ablation and whole-rock analysis both suggest that they have not experienced extensive secondary hydrothermal alteration (Figure 7). Moreover, the geochronological results from these successions (Figure 6) agree with the proposed depositional age for the unit (Kendall et al., 2009). Temperature constraints for this section are within the oil window and diagenetic zone (Figure 2, 3, and 4).~~

Commented [DS109]: Reviewer 2:
Migrating fluids are inferred as cause for isotopic resetting beneath 900m depth. Can these fluids be traced by veins, mineralizations, crystal zonations or else? If so,
can direct thermometry or other geochemical characterization be applicable of such? Has this been observed and considered in any previous study of the site? Indifferent of negative or positive answers to these questions, the matter should be mentioned in the manuscript.

Commented [DS110R109]: Migrating fluids have been observed by oil inclusions in veins cross-cutting the Derim Derim, Bessie Creek Sandstone, as reported in previous studies (Volk et al., 2005; Dutkiewicz et al., 2004). The petrographic textures of the reset shales are also more crystalline when compared to the unreset samples (now provided high-res SEM images in the revision).

Commented [DS111]: Reviewer 2: Generally, chapter 5-8 contains multiple repetitions which can be slimmed. The sentence starting with “This event..” is one of those that includes statements already appearing repeatedly up to this point in the manuscript. Contains statements repeated from previous sections, but if this has the function of a concluding section it should work.

Commented [DS112R111]: Have now been rewritten for clarity.

~~Shale samples sourced from deeper than 900 m in Altree 2, however, preserve evidence for a late-stage, hydrothermal event. Firstly, samples from this depth display foliated and crystalline morphologies that may indicate secondary processes. This is further evinced by the significant relationships shown by alteration proxies for samples from the Lower Velkerri Formation (Figure 7). The Rb–Sr ages yielded from this subset of samples are younger than the depositional ages for the unit dated through Re–Os geochronology (Kendall et al., 2009). Instead, they reflect the age of the Derim Derim Dolerite sourced at 1696 m down-hole (Nixon et al., 2021; Yang et al., 2020). As a result, the secondary event experienced by the Lower Velkerri Formation is likely induced by the emplacement of this mafic intrusion. Further, this depth threshold is where multiple thermal maturation proxies (Figure 2, 3 and 4) suggest that these rocks have experienced temperatures in the anchizone and overmature gas window. These indicators suggest that source rocks within this interval may have experienced palaeotemperatures of at least 150°C (Dellisanti et al., 2010; Frey and Merriman, 1999; Hunt, 1995; Welte and Tissot, 1984). Interestingly, this is in good agreement with evidence from aqueous fluid inclusions in quartz veins within the Derim Derim Dolerite which suggest that hydrocarbons from the Velkerri Formation migrated in the cooling sill at similar temperatures ca. 130°C (Dutkiewicz et al., 2004).~~

7 Modelled Predictions of the Geothermal Aureole Induced by the Derim Derim Dolerite

Resetting of Rb–Sr geochronology and overmaturation of hydrocarbons in the ~~Lower Velkerri Formation~~Kalala Member within the Altree 2 well implies the presence of a secondary ~~thermal and/or~~ hydrothermal aureole extending ca. 800 m away from the Derim Derim Dolerite sill, which is intersected at present day depth 1696 m~~. This event was responsible for the maturation of organic matter into the gas window, mobilisation of trace elements, and resetting the Rb–Sr chronometer in the Lower Velkerri Formation~~. One-dimensional thermal modelling for a sill thickness of 75 m in the Mesoproterozoic suggests temperatures exceeding the oil window over 120°C (Tissot et al., 1974; Waples, 1980) only extended ca. ~~600~~700 m from the intrusion (Figure ~~8A~~9A).

Samples at present day depths of 938 m and 1220 m yield Rb–Sr ages corresponding to emplacement timing of the Derim Derim Dolerite (Nixon et al., 2021; Yang et al., 2020), which suggests that the intrusion caused the chronometer to reset~~.~~ or induced a second mineralisation of clay phases. Predicted temperatures experienced by the shallowest reset sample, however, are lower than the inferred closure temperatures for observed K–Ar and Rb–Sr in sheet silicates (Dodson, 1973; Tillberg et al., 2020; Torgersen et al., 2015; Yoder and Eugster, 1955). In a scenario in which a sill of thickness 75 m was intruded below samples, rocks from present day depth of 938 m are only predicted to have

Commented [DS113]: Reviewer 1: Re-phrase: "which as intersected at present day depth 1696 m.".

Commented [DS114R113]: Done.

Commented [DS115]: Reviewer 1: or induced a second mineralization event?

Commented [DS116R115]: Done.

experienced maximum heating to ca. 110°C (Figure ~~8C~~9C), with temperatures exceeding 100°C for a duration of only ca. ~~50~~150 ka (Figure ~~8B~~9B).

Additionally, the eruption of lavas from the Kalkarindji LIP (Evins et al., 2009; Glass and Phillips, 2006; Jourdan et al., 2014), within the same vertical profile offer an intriguing opportunity to evaluate thermal resistance of the Rb–Sr system in shale-hosted clays in different conditions. Basaltic lavas of the ca. 510 Ma Cambrian Kalkarindji LIP (Evins et al., 2009; Glass and Phillips, 2006; Jourdan et al., 2014) are preserved above Proterozoic sedimentary rocks in the Altree 2 well. Furthermore, regional apatite fission track data suggest that the thermal pulse induced during this LIP extrusion were short-lived but sufficient (> 190°C) to anneal tracks in the upper ~500 m of the basin ~~(Nixon et al., submitted).~~(Nixon et al., 2022). However, the shallowest samples taken in this study (at depths 415 m, 520 m, and 696 m) did not have their Rb–Sr isotopic system disturbed despite experiencing such temperatures from this reheating event. Consequently, the thermal profile for the sample at 415 m depth provides a minimum closure temperature constraint for short-lived conditions which have not reset the Rb–Sr chronometer in these (presumably) dry shales over 800 million years after the Derim Derim dolerite intrusion. Interestingly, the Cambrian palaeotemperatures imposed by the Kalkarindji lavas ~~(> 190°C; Nixon et al., submitted) are notably higher than Mesoproterozoic palaeotemperatures reached by samples with Rb–Sr ages reset by the Derim Derim Dolerite (ca. 110°C; Figure 8A and 8B~~(Nixon et al., 2022) are notably higher (> 190°C) than Mesoproterozoic palaeotemperatures reached by samples with Rb–Sr ages reset by the Derim Derim Dolerite (ca. 120°C; Figure 9A and 9B).

Such disparity suggests that the presence of fluid (either connate, or sourced from the intrusion), rather than just temperature, is likely to play a critical role in determining whether the Rb–Sr record in a shale is reset. As such, the geochemical system in shales within the aureole may be disturbed at lower temperatures, as trace and rare earth elements are more easily mobilised in hydrothermal fluid systems (Li et al., 2019; Nebel, 2014; Poitrasson et al., 1995; Villa, 1998; Williams-Jones et al., 2012).

~~8 Significance of Constraining *In Situ* Rb–Sr Dating on Proterozoic Shales~~

8 Conclusion

We show that the Velkerri Formation shales intersected by the Altree 2 well ~~preserved the presence~~preserve evidence of an elevated Mesoproterozoic thermal gradient ~~in the~~through an ~800 m ~~surrounding an~~ thick section away from the intrusion of ~~the~~a Derim Derim Dolerite sill (Figure ~~8~~3, 4, and 9). *In situ* Rb–Sr isotopic ages from the ~~Upper~~Wyworrie and ~~Middle Velkerri Formation~~Amungee Members above this hydrothermal aureole yielded ages (Figure 6~~)~~ ~~overlapping with its~~ and 8) within error of their depositional ~~window~~age (Kendall et al., 2009)~~,~~. In addition, unaltered trace element compositions (Figure 7) and petrographic relationships ~~which~~ indicate that the shales preserve an early-diagenetic origin (Figure 5 and Supplementary Material). However, the ~~Lower Velkerri Formation is~~older Kalala Member that lies within the ~~extent of this secondary overprint~~hydrothermal aureole yielded ~~Rb–Sr~~ younger Rb–Sr ages (Figure 6 and 8) consistent with the age of the Derim Derim Dolerite (Ahmad and Munson, 2013; Bodorkos et al., ~~2020~~2022; Nixon et al., 2021; Yang et al., 2020). Samples from this subset also recorded perturbed trace element signatures (Figure 7) as well as fissile, foliated, and crystalline illite morphologies (Figure 5 and Supplementary Material). ~~Importantly, this~~This interval corresponds with disturbed thermal maturity indicators (Figure 2, 3, and 4), suggesting that the Rb–Sr system is stable up to the maturation oil window and reset when the kerogen is overmature. Thermal modelling of the Derim Derim Dolerite suggests that a 75 m thick intrusion at the base of the Altree 2 well would have significantly elevated temperatures within 800 m of the sill, driving kerogen into the gas window, mobilising trace elements and resetting the Rb–Sr isotopic system in the ~~Lower Velkerri Formation~~Kalala Member.

Commented [DS117]: Reviewer 1: crystalline illite morphologies

Commented [DS118R117]: Done.

~~Furthermore, thermal maturation indicators show that the Lower Verlkerri Formation experienced palaeotemperatures of at least 110°C (Dellisanti et al., 2010; Espitalié, 1986; Frey and Merriman, 1999; Hunt, 1995; Welte and Tissot, 1984). Along with elevated temperature, evidence of fluid-driven reactions is invoked as an important process in the perturbation of these shales. Consequently~~In conclusion, we show that the *in situ* Rb–Sr dating of the Velkerri Formation combined with common hydrocarbon maturity proxies can help reveal the thermochronological history of Proterozoic argillaceous rocks~~ (Figure 9).~~. When used in tandem, these methods can constrain the age of deposition as well as subsequent secondary, late-stage geological events. Importantly, we demonstrate that this technique can aid sedimentary-hosted resource exploration, as hydrothermal overprints can be identified and dated as previously demonstrated in Subarkah et al. (2021). Specifically, for hydrocarbon exploration, we show that the thermo-kinetic parameters of shale-hosted Rb–Sr isotopic system in hydrothermal settings can coincide with the maturation of kerogen into the gas window (Dodson, 1973; Espitalié, 1986; Kubler, 1967).

9 Figure Captions

Figure 1A, left. Schematic stratigraphy and geochronological summary of the Roper Group (Abbott et al., 2001; Jackson et al., 1999; Kendall et al., 2009; Southgate et al., 2000; Subarkah et al., 2021; Yang et al., 2020). B, right. Sample location and depth to basement map for the McArthur Basin adapted from Frogtech Geoscience (2018).

Figure 2. Summary of reprocessed down-hole well log data for Altree 2.

Figure 3. Covariation between T$_{max}$ values from pyrolysis analysis and illite crystallinity KI in the Velkerri Formation. An increase in T$_{max}$ coincide with a decrease in KI, suggesting that these proxies are both mainly sensitive to changes in palaeotemperature.

Figure 4. ~~Kerogen characterisation of the Velkerri Formation based on organic geochemical parameters (Espitalié et al., 1985; Espitalié et al., 1977). Note that the Lower Velkerri Formation primarily hosts gas-prone kerogen. Upper Velkerri Formation = blue, Middle Velkerri Formation = teal, Lower Velkerri Formation = pink~~Calculated vitrinite reflectance (VR$_{CALC}$) data down-hole modelled from T$_{Max}$, MPR, MPDF, and bitumen reflectance data compiled in this study (Capogreco, 2017; Cox et al., 2016; Jarrett et al., 2019b; Lemiux, 2011; NTGS, 1989, 2009, 2010, 2012; Revie, 2014; Revie et al., 2022). VR$_{CALC}$ from all proxies all indicate an elevation in thermal maturity into the gas window at depths ca. 900 m.

Figure 5. Spectral reflectance MLA maps of samples selected for *in situ* laser ablation analysis in this study overlain on top of their respective BSE images. White dash lines show illite assemblages wrapping around detrital grains and forming cements. Black dash lines show foliation in illite crystals. Black dashed lines show large illite crystals replacing previous clay assemblages. Solid white lines are 100 µm scale bars.

~~Figure 6. Summary of *in situ* Rb–Sr geochronological results from this study. Note that the best dated samples have the better spread in ^{87}Rb/^{86}Sr ratios, as suggested by Nebel (2014).~~

Figure 6. Summary of *in situ* Rb–Sr geochronological results from this study.

Figure 7. Statistical relationships between alteration proxies obtained from this study through laser ablation analysis (A) and whole-rock geochemical data (B) compiled from Cox et al. (2016).

Figure ~~8A~~8. Single-spot ages from samples in this study illustrated by KDE (A), CAD (B), and MDS (C) plots. Note that the population of single-spot ages for samples at depths 415 m, 520 m, and 696 m all overlap with previous Velkerri Formation Re–Os age constraints shown in light pink (Kendall et al., 2009). On the other hand, samples at depth 938 m, and 1220 m are statistically different and instead agree with the Derim Derim Dolerite intrusion ca. 1330–1300 Ma displayed in dark pink (Bodorkos et al., 2022).

Figure 9A. One-dimensional thermal model for sill intrusion of 75 m thickness within the Altree 2 well depicting time steps following emplacement at 0 ka. Sill intrusion and Rb–Sr sample depths have been normalised to palaeodepths with 1~~ km of additional Mesoproterozoic sediments. Median palaeotemperature estimates from T$_{max}$~~.5 km of additional Mesoproterozoic

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The advantage of in situ analysis is to show textural context, so it would be better to show the location of the laser spots on the images of figure 5. This would also show clearly your spatial resolution compared to the fine grain of the samples.

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Commented [DS129]: Reviewer 1: Can the authors explain the differences in the initial 87Sr/86Sr values among the sample set, i.e. ranging from radiogenic to seawater-type?

Commented [DS130R129]: This is calculated from the isochrons. Each samples have a different spread in data, and as such, the initial 87Sr/86Sr value calculated from each isochron (i.e. the y-intercept) will differ.

Commented [DS131]: Editor:
Improve figure 6 by (i) zooming into the data part in each of them rather than plot all diagrams with the same scale; (ii) increase the font size of the number on axis and (iii) ensure that Sr initial value and its uncertainty are quoted with the same number of digits (0.702 ± 0.006, and not ±0.0060).

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sediments (Hall et al., 2021). Median palaeotemperature estimates from VR$_{CALC}$ data from the Altree 2 well have been included for comparison to modelled temperatures. B. Time-temperature profile for sample intervals within the Altree 2 well following intrusions of a sill of 75 m thick.

~~**Figure 9. Summary of the thermochronological history of the Velkerri Formation in Altree 2. Black bars = *in situ* Rb–Sr shale ages. Re–Os shale geochronology from Kendall et al. (2009) and U–Pb dating of the Derim Derim Dolerite intrusion from Yang et al. (2020). Dashed lines = compilation of T_{max} data in this study (Cox et al., 2016; NTGS, 2009, 2010).**~~

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Author Contributions

Darwinaji Subarkah (primary author): Conceptualisation, method development, experimentation, manuscript drafting.

Angus Leslie Nixon: Conceptualisation, computational modelling, manuscript drafting.

Monica Jimenez: Conceptualisation, manuscript drafting.

Alan Stephen Collins: Conceptualisation, primary supervision, manuscript drafting, funding.

Morgan Lee Blades: Sampling, method development, experimentation, manuscript drafting, secondary supervision.

Juraj Farkaš: Conceptualisation, method development, secondary supervision.

Sarah Gilbert: Method development, experimentation, manuscript drafting.

Simon Holford: Manuscript drafting, conceptualisation.

Amber Jarrett: Manuscript drafting, data collection.

12 Competing Interests

The authors declare that they have no conflict of interest.

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