

## Constraining the geothermal parameters of *in situ* Rb–Sr dating on Proterozoic shales and [their](#) subsequent applications

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**Abstract** Recent developments in tandem laser ablation–mass spectrometer technology have [demonstrated capacity for shown to be capable of](#) 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 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 this approach. We then constrained thermal history of these units using common hydrocarbon maturity indicators, and modelled effects of contact heating due to the intrusion of the Derim Derim Dolerite.

*In situ* Rb–Sr dating of mature, oil-prone shales in the diagenetic zone from the Velkerri Formation yielded ages of  $1448 \pm 81$  Ma,  $1434 \pm 19$  Ma, and  $1421 \pm 139$  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 deeper within the borehole were dated at  $1322 \pm 93$  Ma and  $1336 \pm 40$  Ma. These ages are younger than the expected depositional window for the Velkerri Formation. Instead, they are consistent with the age of the Derim Derim Dolerite mafic intrusion intersected 800 m below the 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 [window point](#) in which kerogen from the Velkerri Formation becomes overmature. As a result, the mafic intrusion intersected here is interpreted to have caused kerogen in these shales to enter the gas window, induced fluids that mobilise trace elements and reset the Rb–Sr chronometer. Consequently, we propose that the Rb–Sr chronometer in shales may be sensitive to temperatures of ca. 110°C in hydrothermal reactions but can withstand temperatures of more than 190°C in 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). Therefore it is an effective technique to date processes such as igneous 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 ( $^{87}\text{Rb}$ ) and daughter ( $^{87}\text{Sr}$ ) 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, causing the technique to lose its popularity in recent years (Nebel, 2014).

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., 2021b; Gorojovsky and Alard, 2020a; Hognalm et al., 2017; Redaa et al., 2021a; Yim et al., 2021; Zack and

Hogmalm, 2016). Reactive gasses such as N<sub>2</sub>O and SF<sub>6</sub> can be introduced into a reaction cell between quadrupoles in an LA-ICP-MS/MS system, which permits the online separation of <sup>87</sup>Sr from <sup>87</sup>Rb through the measurement of the mass shifted Sr reaction product (Hogmalm et al., 2017; Redaa et al., 2021a; Zack and Hogmalm, 2016). 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; Gorjovsky and Alard, 2020b; Harrison et al., 2010; Hogmalm et al., 2019; Ribeiro et al., 2021; Rösel and Zack, 2022; Scheibhofer et al., 2022; Simpson et al., 2021; Simpson et al., 2022; Tamblyn et al., 2021).

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. In addition, the initial <sup>87</sup>Sr/<sup>86</sup>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 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., 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.

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 formation waters (Deepak et al., 2022; Isson and Planavsky, 2018; Kennedy et al., 2006; Mackenzie and Kump, 1995; Rafei and Kennedy, 2019; Rafei 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; Rafei 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 [complications/weaknesses](#) 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/maturation–diagenesis](#) via [the transformation of smectite to illite–smectite mixed layer minerals/minerals–S formation](#).

In this study, we dated the Mesoproterozoic Velkerri Formation from [the Roper Group](#) of the McArthur Basin in northern Australia by *in situ* Rb–Sr geochronology and show that clay-mineral recrystallization in these shales occur at similar temperatures 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; Cox et al., 2022; Kendall et al., 2009; Southgate et al., 2000; Subarkah et al., 2021; Yang et al., 2020). Furthermore, the resurgence of interest in the resource potential of the organic-rich Velkerri Formation has also yielded a framework of palaeotemperature data that aim to discern the maturation history of hydrocarbons within the unit (Ahmad and Munson, 2013; Capogreco,

115 2017; Cox et al., 2016; Crick et al., 1988; George and Ahmed, 2002b; Jarrett et al., 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 Atree 2 (Capogreco,  
2017; Cox et al., 2022; Cox et al., 2016; George and Ahmed, 2002b; Jarrett et al., 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).

120 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  
125 traditional kerogen maturation proxies can be a powerful tool for reconstructing the thermochronological evolution  
of Proterozoic basin systems. This approach can [then](#) be applied to aid in hydrocarbon exploration for similar  
settings.

## 2 Geological Background

The Palaeo-to-Mesoproterozoic greater McArthur Basin is an intra-cratonic sedimentary system exposed across  
130 180,000 km<sup>2</sup> 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;  
135 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 sequences](#) ~~thickest~~  
[here](#) (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; Jackson et al.,  
140 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; 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  $1589 \pm 3$  Ma and  $1577 \pm 56$  Ma, respectively (Page et al., 2000; Subarkah et al., 2021). The unconformity between the Roper Group and the ~~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  $1492 \pm 4$  Ma and  $1493 \pm 4$  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  $1313 \pm 47$  Ma (Yang et al., 2018) and the age of crosscutting Derim Derim dolerite intrusions at  $1313 \pm 1$  Ma, ~~and~~  $1324 \pm 4$  Ma, ~~and~~  $1327.5 \pm 0.6$  Ma (Bodorkos et al., ~~2022~~2020; Yang et al., 2020).

~~Mature~~The Velkerri Formation within the Roper Group is the focus of this study and mature organic-rich shales from the Velkerri Formation ~~this unit~~ have been dated by Re–Os analysis at  $1417 \pm 29$  Ma and  $1361 \pm 21$  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 mudstones and siltstones that coarsens-up into the cross-bedded Moroak Sandstone and Sherwin Ironstone (Abbott et al., 2001). The 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 ~~members (from bottom to top, the KalalaKalalaWyworrie, Amungee, and Wyworrie Kalala-Members)~~ based on ~~their~~ variations in total organic carbon (TOC) content, gamma ray response, 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 [Roper Group](#) [Wilton Package](#). Mafic sills of the Derim Derim Dolerite widely intrude all units in the Roper Group at ca. 1330–1300 Ma, with the oldest intrusions likely contemporaneous with the end of sedimentation in the basin (Ahmad and Munson, 2013; Bodorkos et al., 2020; 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~~ [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 Atree 2 well drilled in the Beetaloo Sub-basin [was](#) chosen for this study as it intersects the entirety of the Velkerri Formation (Figure 2). In addition, the well also intersected lavas of the Kalkarindji LIP directly 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; Cox et al., 2022; Cox et al., 2016; Cox et al., 2019; George and Ahmed, 2002b; Jarrett et al., 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 (NRS) and Density (RHOB) of the Atree-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 % and RHOB of around 2.5  $\text{g}/\text{cm}^3$ . 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

195 API, NRS > 0.20 and < 0.25 m<sup>3</sup>/m<sup>3</sup> and RHOB between 2.5 and 2.53 g~~g~~g/cm<sup>3</sup>. 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<sup>3</sup>/m<sup>3</sup> and RHOB > 2.53 g~~g~~g/cm<sup>3</sup> 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 g~~g~~g/cm<sup>3</sup>. This indicates a competent lithology in the GR with a  
200 gap between the neutron and density curves. In addition, T<sub>max</sub> data ~~were also~~ ~~was~~ ~~were~~ ~~also~~ collated to discriminate  
the hydrocarbon maturation levels downhole. From this, a shift in hydrocarbon potential and T<sub>max</sub> gradients were  
identified at around 900 m (Figure 2), ~~where~~ ~~were~~ kerogen enters the gas window and becomes overmature. Five  
shale chips were then sampled from the Velkerri Formation in Atree 2 at depths of 415 m, 520 m, 696 m, 938 m,  
and 1220 m for further characterisation.

205 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  
210 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). The laser set-up used in this study is provided in the Supplementary Material. Laser ablation  
215 data and error correlations were processed using the LADR software package (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 signatures were also  
culled or cropped during the processing of each ~~analysis~~ ~~analyses~~ to aid in ensuring spot homogeneity. The <sup>87</sup>Rb  
decay constant used was 0.000013972 ± 4.5e-7 Myr<sup>-1</sup> following Villa et al. (2015). Isochron and single-spot ages  
220 were calculated with ISOPLOTR (Vermeesch, 2018). Single-spot ages were calculated using the isochron intercept  
as their initial <sup>87</sup>Sr/<sup>86</sup>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~~



225 multidimensional scaling (MDS) graphs (Vermeesch, 2013) ~~were also, and radial plots (Galbraith, 1990) were also done-constructed~~ using ISOPLOTR (Vermeesch, 2018) to differentiate between the population of single-spot ages from each sample.

230 The ~~phlogopite~~~~phlogopite~~~~phlogopite~~ nano-powder Mica-Mg (Govindaraju et al., 1994) was used as the primary reference material and its natural mineral equivalent MDC from ~~the Ampandrandava mine~~~~Bekily 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.

235 When anchored to a  $^{87}\text{Sr}/^{86}\text{Sr}$  initial ratio =  $0.72607 \pm 0.00363$  as reported by Hogmalm et al. (2017), MDC yielded an age of  $524 \pm 7$  Ma. This is within error of the published mean age of Mica-Mg at  $519 \pm 7$  Ma (Hogmalm et al., 2017). In addition, the independent reference material GL-O gave an age of  $96 \pm 4$  Ma, accurate to its published ~~K-~~~~Ar~~ age of  $95 \pm 1.593 \pm 4$  Ma (Charbit et al., 1998; Derkowski et al., 2009). It should be noted that this age is younger than the tuff-horizon age of the GL-O host rock, dated at  $113 \pm 0.3$  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).

240 Glass ~~standard~~~~standards~~ 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<sup>2</sup> > 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).

245 One-dimensional thermal modelling of the Atree 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 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

250 conducted to replicate maximum thermal conditions calculated in the well from the thermal maturity data, where  
palaeotemperatures suggest ~~that the~~ Wyworrie and Amungee Members experienced significant additional  
sedimentary cover ~~in~~present during 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),  
255 ~~while all post-Mesoproterozoic units were excluded., 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 ~~28682368~~ m, in  
accordance with adjusted burial depths during the Mesoproterozoic. As sill thickness is unconstrained within the  
Atree 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  
260 modelling parameters and petrophysical properties are provided in the Supplementary Material Table S2 and Table  
S3.

## 4 Results

### 4.1 Compilation of legacy data

265 All legacy data are compiled in the Supplementary Material and were checked for quality before 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). 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<sub>max</sub> and Hydrogen Index.  
270 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<sub>max</sub> values (< 380°C) present. Extremely low T<sub>max</sub>  
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<sub>max</sub> results compiled in this study ranges between 384°C to 502°C with a  
mean of 433°C (st. dev. = 17). TOC content in the Velkerri Formation varies from 0.07% to 8.07%, averaging at  
275 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 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 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, including biotite, chlorite, clinocllore, 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 spaced 1 – 2 cm apart may yield different results. In addition, the targeted areas for MLA [areis](#) 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 [difficultenigmatic](#). 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 Wyworrie and Amungee Members gave ages within error of each other. The sample from 415 m depth was dated at  $1448 \pm 81$  Ma. Next, the mudstone analysed from 520 m depth yielded an age of  $1434 \pm 19$  Ma. Thirdly, the shale sample studied from 696 m depth resulted in an age of  $1411 \pm 139$  Ma. A Kalala Member shale chip from 938 m at depth was dated at  $1322 \pm 93$  Ma. Another sample from this member, towards the boundary with the underlying Bessie Creek Sandstone at depth 1220 m resulted in an age

of  $1336 \pm 40$  Ma. The range of precision from these Rb–Sr ages are primarily constrained by a substantial spread in  $^{87}\text{Rb}/^{86}\text{Sr}$  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  $^{87}\text{Rb}/^{86}\text{Sr}$  ratios (0 – 50) whilst the other two samples preserved a range of  $^{87}\text{Rb}/^{86}\text{Sr}$  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).

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 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 Atree 2 well is sufficient to produce a thermal aureole reaching temperatures  $> 110\pm 40^\circ\text{C}$ , ca. 800 m above the top contact of the sill (Figure 9A). Maximum palaeotemperatures recorded in the 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., 2022)(Nixon et al., 2022submitted). The resultant maximum thermal profile is consistent with  $T_{\text{max}}$  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.  $120\pm 10^{\circ}\text{C}$ . 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 9B).

Method	Apatite	Biotite	Chlorite	Clinochlore		Dolomite	Glauconite	Illite	Kaolinite	Magnetite	Montmorillonite	Orthoclase	Pyrite	Quartz	Siderite	Zircon	Plagioclase
				0.00	0.00												
Bulk XRD	0.00	0.00	0.00	0.00	0.00	0.25	0.82	34.05	21.25	0.36	1.79	13.33	0.28	26.13	1.76	0.00	0.00
MLA Map	0.00	1.22	1.3322	0.00	0.00	0.00	0.00	35.52	7.45	0.89	9.05	11.48	0.40	23.93	0.00	0.02	4.39
Bulk XRD	0.00	0.00	0.00	0.00	0.00	0.37	2.35	43.28	17.14	0.38	2.01	10.01	0.74	23.67	0.05	0.00	0.00
MLA Map	0.00	0.07	0.0840	0.00	0.00	0.00	0.00	36.51	7.11	0.00	0.04	4.08	0.24	47.94	0.00	0.00	0.85
Bulk XRD	0.00	0.00	0.00	0.00	0.00	0.21	1.53	27.59	2.07	0.00	1.49	13.40	4.11	45.02	0.00	0.00	4.57
MLA Map	0.31	0.93	0.0640	0.00	0.00	0.00	0.00	18.48	0.00	0.00	4.00	8.27	4.47	60.88	0.00	0.00	1.41
Bulk XRD	0.00	0.00	0.00	0.00	0.00	0.53	1.36	27.03	6.99	0.33	1.16	11.32	1.49	43.28	0.01	0.00	6.50
MLA Map	1.2	0.00	0.0640	0.00	0.00	0.00	0.00	22.13	5.46	0.00	0.00	3.37	1.60	57.79	0.00	0.00	6.90
Bulk XRD	0.00	0.00	0.00	0.00	0.00	0.43	1.04	39.36	13.99	0.42	1.66	7.32	0.26	33.56	0.10	0.00	1.86
MLA Map	0.00	0.01	0.0140	0.00	0.00	0.05	0.00	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 <sup>2</sup>	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

335

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. All values are in weight percent. B. Covariation between the mineral phases categorised by both methods.

### 5 Thermal Maturity of the Velkerri Formation

340 Geochemical and mineralogical-based thermal maturity indicators collected via Rock-Eval studies and bulk XRD analyses were compiled in this study in order to establish a vertical profile of the Velkerri Formation 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

345 Kübler index (KI) is determined by the 001-reflection 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 multiple factors other than burial-related heating and therefore struggle to resolve absolute quantitative palaeotemperatures. 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,

350 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 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

355 indicators need to be treated with caution when applied independently and are more suitable as qualitative



discriminators as opposed to absolute 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 the thermal histories of sedimentary 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 Atree 2 well (Figure 3). In our compilation, samples with immature kerogen ( $T_{\max} < 435^{\circ}\text{C}$ ) correspond to rocks in the diagenetic zone ( $\text{KI} > 0.45^{\circ}\Delta 2\theta$ ). This relationship is true in similar studies and generally translates to palaeotemperatures of ca.  $100^{\circ}\text{C}$  (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 ( $435^{\circ}\text{C} < T_{\max} < 465^{\circ}\text{C}$ ) show a wide range of KI values between 0.39 and  $0.65^{\circ}\Delta 2\theta$  (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  $150^{\circ}\text{C}$  (Árkai et al., 2002; Frey and Merriman, 1999; Kosakowski et al., 1999; Welte and Tissot, 1984).

On the other hand, the sample displaying over-mature kerogen ( $T_{\max} > 465^{\circ}\text{C}$ ) corresponds to the smallest KI value (Figure 3) of  $0.36^{\circ}\Delta 2\theta$  (Dellisanti et al., 2010). These values commonly define the gas window and the anchizone, corresponding to palaeotemperatures of ca.  $200^{\circ}\text{C}$  (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).

385 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 (Radke et al., 1982; Wilhelms et al., 1998), 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 (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. 390 900 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 strong correlation between them, suggesting that the proxies used in this study primarily recorded changes in palaeotemperature as opposed to other possible variables. Notably, five different, independent, source-rock maturation proxies statistically agree and recorded similar step-wise increase in thermal history down-hole. As such, 395 we investigated five samples approaching the geothermal anomaly in the 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

400 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) ~~and radial~~ plots of these results ([Figure 8A and 8D](#)) show that the distribution of single-spot ages from samples shallower than 900 m largely overlaps with the Re–Os ~~time-age~~ constraint ([Figure 8A; light pink](#)) for the Velkerri Formation (Kendall et al., 405 2009). On the other hand, the population of single-spot ages from shales deeper than 900 m ([Figure 8A and 8D](#)) instead ~~agrees~~ with the ~~age-time window for the~~ age of the Derim Derim Dolerite ([Figure 8A; dark pink](#)) [intrusion ca. 1330–1300 Ma](#) ([intrusion event](#)) (Ahmad and Munson, 2013; Bodorkos et al., 2020; 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~~ ~~Both~~ ~~of~~ ~~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 ~~statistically similar~~ cluster, which in turn coincides with the ~~age of the~~ Derim Derim ~~Dolerites~~ ~~Dolerites event~~ (Ahmad and Munson, 2013; Bodorkos et al., 2020; Nixon et al., 2021; Yang et al., 2020). Consequently, the Rb–Sr ~~shale results ages of shales~~ ~~ages~~ from this section ~~may not be~~ ~~are unlikely to~~ ~~date~~ ~~date~~ ~~indicative of the~~ deposition of the Velkerri Formation, but instead reflect a late-stage hydrothermal resetting induced by the intrusion.

**Commented [AC1]:** CAD doesn't really use the K-S statistic – you construct a

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). 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). Primary sedimentary structures such as 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). Moreover, the ages from these samples are all in agreement with the deposition of the Velkerri Formation dated at  $1417 \pm 29$  Ma by Re–Os geochronology (Kendall et al., 2009), suggesting that the majority of illite formed relatively soon after sediment deposition.

Nevertheless, we also 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 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). These support proxies further evidence support an interpretation that the se ages from produced here can be interpreted as form a minimum depositional age for the unit, recording an early diagenetic event as opposed to a late-stage secondary overprint. Furthermore, temperature constrains for the Velkerri Formation at depths 390–900 m suggest that they are well-within the oil window (Figure 3 and 4). As a result, we propose that 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 Figure S2D-E). Clay minerals in sample from the 938 m sample depth are fissile and foliated (Figure 5). In addition, pyrite and apatite can be observed overgrowing illite and chlorite. Moreover, illite grains from the Kalala Member shale at 1220 m depth depths are notably larger and crystalline (Figure 5 and Figure S2D-E), with features inconsistent with an early diagenetic origin (and Figure S2D-E). Clay minerals were also found interlocking with quartz overgrowth and appear to replace earlier assemblages (Figure 5 and Figure S2D-E).

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 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). These alteration indicators are further evidence that the Kalala Member at depths below 900 m experienced a late-stage secondary heating event, as trace elements are more readily mobilised in 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, thermal indicators from this interval suggest that kerogen in these shales are thermally overmature (Figure 3 and 4). Previous studies have shown that the source rocks in the Velkerri Formation became overmature only when affected by magmatic events (Crick et al., 1988; George and Ahmed, 2002a),(Crick et al., 1988; George and Ahmed, 2002b). As such, it is plausible that the Derim Derim Dolerite intrusion intersected in this well has hasve prompted-imposed a hydrothermal alteration footprint onto its-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.

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

Resetting of Rb–Sr geochronology and overmaturation of hydrocarbons in the Kalala Member within the Atree 2 well implies the presence of a secondary hydrothermal aureole extending ca. 800 m away from the Derim Derim Dolerite sill, which is intersected at present day depth 1696 m. 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. ~~700~~600 m from the intrusion (Figure 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

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

495 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 Atree 2 well. Furthermore, regional apatite fission track data suggest that the thermal pulse induced  
500 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., 2022](#)).([Nixon et al., submitted2022](#)). 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  
505 these (presumably) dry shales over 800 million years after the Derim Derim dolerite intrusion. Interestingly, the  
Cambrian palaeotemperatures imposed by the Kalkarindji lavas (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~~140°C; Figure 9A and 9B).

Such disparity suggests that the presence of fluid (either connate, or sourced from the intrusion), rather than just  
510 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 ~~Conclusion~~Conclusions

515 ~~We consequently, we~~ ~~We show-shot-~~ that the Velkerri Formation shales intersected by the Atree 2 well  
~~preservepreserved the presence-of-evidence of~~ an elevated ~~Mesoproterozoic~~ thermal gradient ~~through an in a~~ ~800 m

thick section away from the overlying anthe intrusion of aathe Derim Derim Dolerite sill (Figure 3, 4, and 9). *In situ* Rb–Sr isotopic ages from the Wyworrie and Amungee Members above this hydrothermal aureole yielded ages (Figure 6 and 8) ~~within overlapping with its depositional window~~ within error of their depositional 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 ~~petrography and geochemistry~~ origin (Figure 5 and Supplementary Material). However, the ~~older~~ Kalala Member that ~~lies within the hydrothermal aureole is within the extent of this secondary overprint~~ yielded 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; 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). ~~This~~ ~~Importantly,~~ ~~†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 Atree 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 Kalala Member.

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. 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 Atree 2.

545 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.

550 Figure 4. Calculated vitrinite reflectance ( $VR_{\text{CALC}}$ ) data down-hole modelled from  $T_{\text{Max}}$ , 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).  $VR_{\text{CALC}}$  from all proxies all indicate an elevation in thermal maturity into the gas window at depths ca. 900 m.

555 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  $\mu\text{m}$  scale bars.

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).

560 Figure 8. Single-spot ages from samples in this study illustrated by KDE (A), CAD (B), ~~and MDS (C)~~, and radial plots. (~~D~~). 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 ~~agrees~~ with the ~~time of Derim Derim Dolerite intrusion ca. 1330–1300 Ma displayed in dark pink~~ event (Bodorkos et al., ~~2022~~2020).

565 Figure 9A. One-dimensional thermal model for sill intrusion of 75 m thickness within the Atree 2 well depicting time steps following emplacement at 0 ka. Sill intrusion and Rb–Sr sample depths have been normalised to palaeodepths with ~~1.5 km of additional Mesoproterozoic sediments (Hall et al., 2021)~~. ~~km of additional Mesoproterozoic sediments~~. Median palaeotemperature estimates from  $VR_{\text{CALC}}$  data from the Atree 2 well have been included for comparison to modelled temperatures. B. Time-temperature profile for sample intervals within the Atree 2 well following intrusions of a sill of 75 m thick.

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\[https://github.com/jarredlloyd/PowerShell\\\_LADR\\\_errorcorrelation\\\_workaround\]\(https://github.com/jarredlloyd/PowerShell\_LADR\_errorcorrelation\_workaround\).](#)

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## 11 Author Contributions

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

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

Monica Jimenez: Conceptualisation, manuscript drafting.

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## 12 Competing Interests

595 The authors declare that they have no conflict of interest.

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