Unraveling the histories of Proterozoic shales through *in situ* Rb-Sr dating and trace element laser ablation analysis

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**ABSTRACT**

Authigenic components in marine sediments are important archives for past environment reconstructions. However, defining reliable age constraints and assessing the effects of post-depositional overprints in Precambrian sequences are challenging. We demonstrate a new laser-based analytical approach that has the potential to rapidly and accurately evaluate the depositional and alteration histories of Proterozoic shales. Our study employs a novel application of *in situ* Rb-Sr dating coupled with simultaneous trace-element analysis using reaction-cell laser ablation–inductively coupled plasma–tandem mass spectrometry (LA-ICP-MS/MS). We present results from shales sourced from two wells in the Proterozoic McArthur Basin, northern Australia. These rocks have been widely used by previous studies as a key section for ancient biogeochemical and paleo-redox reconstructions. Shales from well U5 yielded initial $^{87}$Sr/$^{86}$Sr ratios, Rb-Sr ages, and rare earth element plus yttrium (REEY) patterns similar to those of a dolerite sampled from the same core. We propose that the U5 samples chronic hydrothermal alteration instigated by the dolerite intrusion. In contrast, a correlative shale from well U6 yielded an age consistent with the expected depositional age (1577 ± 56 Ma) with REEY and initial $^{87}$Sr/$^{86}$Sr ratios similar to ca. 1.5 Ga seawater. We suggest that this sample records the minimum depositional age and early marine diagenetic history for this unit. This new technique can date Proterozoic shales quickly, cheaply, and with minimum sample preparation. Importantly, ages are triaged to differentiate between those recording primary marine versus secondary processes. This novel approach provides a potentially powerful tool for dating and fingerprinting the vast array of ancient marine shales for further studies of Earth systems through deep time.

**INTRODUCTION**

Analyses of the sedimentary record have been integral in constraining how Earth systems have evolved over geological time. For example, geochemical proxies of seawater paleo-redox conditions reveal key periods of fluctuating oxygen levels that are intrinsically linked to the development of life (e.g., Lyons et al., 2014; Plavnik et al., 2015). Furthermore, the radiogenic $^{87}$Sr/$^{86}$Sr isotope record of seawater inferred from marine carbonates reflects the balance between $\text{Sr}$ input from continental weathering versus that from submarine hydrothermal systems, reflecting global-scale tectonic changes (Kuznetsov et al., 2014). However, these archives are meaningful only if one is able to accurately date and assess the primary compositions of the rocks investigated. These prerequisites are further complicated by the lack of a diverse faunal record in the Proterozoic, restricting the use of biostratigraphy to constrain depositional ages. Consequently, an array of other chronological techniques has been developed to date Precambrian sedimentary rocks.

Shales are common throughout the Precambrian, but dating sedimentary packages dominated by shales has proven to be difficult. Re-Os dating of organic-rich shales is a powerful technique for attaining depositional ages (Ravizza and Turekian, 1989; Kendall et al., 2009). However, this method has limitations. There is a low abundance of Re in natural environments, such that many shales are too Re-poor to date (e.g., Rainbird et al., 2020). In addition, the method is costly and time consuming and yields hard-won but limited data. Sample intervals also commonly represent deposition over tens to hundreds of centimeters vertically and as much as several kilometers laterally (e.g., Kendall et al., 2009; Rainbird et al., 2020). Detrital zircons are useful for analyzing provenance and establishing maximum depositional ages (e.g., Yang et al., 2019) where sand units are available. Dating volcanic beds in sedimentary units is the most precise method to obtain depositional ages (e.g., Southgate et al., 2000), but many sequences are devoid of such lithologies. Similarly, direct dating of intrusions in sedimentary rocks or early diagenetic minerals such as xenotime (Rasmussen et al., 2004) can provide minimum depositional ages of sediments but rely on specific geological conditions to be met.

Alternatively, the Rb-Sr isotopic system can date deposition (Compston and Pidgeon, 1962; Nebel, 2014) and early diagenetic illite formation in shales (Gorokhov et al., 2001). However, the past limitation of beta-decay-system chronometers such as $^{87}$Rb-$^{87}$Sr was that daughter and parent isotopes could not be differentiated by traditional mass spectrometry. Instead, an arduous process of whole-rock digestion and column chromatography, requiring large sample volumes, was needed. This restricted the number of analyses undertaken and also prohibited effective identification and isolation of detrital or diagenic phases, causing the technique to lose popularity. The development of tandem inductively coupled plasma–mass spectrometry (ICP-MS/MS) instruments allows for many of these challenges to be overcome (Zack and Hogmalm, 2016; Redaa et al., 2021). Introduction of a reactive gas into a reaction cell between the two quadrupoles in an ICP-MS/MS system enables the online separation of $^{87}$Sr from $^{86}$Rb via
The northern Australian Proterozoic McAr
thur Basin is intra-cratonic and consists of four
unconformity-bound sedimentary packages
(Ahmad and Munson, 2013). U-Pb thermal
ionization mass spectrometry (TIMS) analyses
of the same suite sampled at locations >200 km
apart yielded ages of 1327.5 ± 0.6 Ma (Bodor-
kos et al., 2020) and 1312.9 ± 0.7 Ma (Yang
et al., 2020), respectively.

We sampled the Collara Subgroup in two
wells: UR5 and UR6 (Fig. 1A). Shale samples
analyzed in this study are from the Gibb and
Wooden Duck Members (Mainoru Formation;
samples UR6_269 and UR5_578, respectively)
and the Jalboi Formation (sample UR5_139).
Shales from well UR5 were picked to con-
strain the alteration aureole of the Derim Derim
intrusion.

ANALYTICAL METHODS
The mineralogy and petrography of the
shales were characterized by energy-dispersive
X-ray spectroscopy (EDS) mapping with Nano-
min software (Rafiei et al., 2020) at Macquarie
University (Sydney, Australia) following the
approach of Rafiei et al. (2020) complemented
with bulk powder X-ray diffraction (XRD).
The dolerite was mapped for its petrographic
textures and elemental composition using a scanning
electron microscope at Adelaide Microscopy
(Adelaide, Australia; see the Supplemental
Material). Laser analyses were performed at
Adelaide Microscopy following Redaa et al.
(2021). Phlogopite nano-powder Mica-Mg
as well as its natural mineral crystal (MDC)
sourced from Bekily, Madagascar (Govinda-
raju et al., 1994), were used as standards for
data normalization. In addition, an illite pressed
designed pellet from Fithian, Illinois, USA (Kra-
lik, 1984), was analyzed as a complementary
in-house comparison to assess possible matrix
differences between the phlogopite standards
and the illite-rich shales analyzed in this study.
Finally, the morphology and structure of laser
craters in standards and samples were imaged
using an Olympus FV3000 confocal microscope
(Fig. S5 in the Supplemental Material). Method-
ologies are extensively discussed in the Supple-
mental Material.

RESULTS
The pit-depth profiles show that samples
analyzed in this study have similar ablation
characteristics to the Mica-Mg nano-powder
standard and the Fithian illite pellet as opposed
to the MDC mineral flake (Fig. S5; see the

Supplemental Material. Extended methods and
dataset. Please visit https://doi.org/10.1130/
GEOL.S.16569531 to access the supplemental material,
and contact editing@geosociety.org with any questions.
Supplemental Material). Semiquantitative and microscale identification of the studied shales are reported in Figure 2. The Gibb Member shale (sample UR6_269) gave an age of 1577 ± 56 Ma with initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7046 ± 0.0073. The Derim Derim Dolerite (sample UR5_229) yielded an age of 1347 ± 47 Ma with initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio: 0.7260 ± 0.023. Finally, the Wooden Duck Member shale (sample UR5_578) had an age of 1322 ± 49 Ma (initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio: 0.7339 ± 0.015). REEY values from all shale samples were normalized to those of sample UR_269 because this is interpreted to be the best-preserved shale, with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio reflective of ca. 1.5 Ga seawater (Fig. 3) and the least-altered mineralogy (Fig. 2). All remaining samples show a normalized light REE (LREE) depletion (Fig. 3B). The Jalboi Formation shale is located closest to the dolerite intrusion and has REEY patterns most similar to those of the dolerite.

**DISCUSSION**

The majority of illite in Proterozoic shales of the McArthur Basin is believed to have formed during early marine diagenesis via reverse weathering processes in equilibrium with paleo-seawater, as opposed to being detrital products of continental weathering from soils like those commonly found in Phanerozoic shales (Rafiei and Kennedy, 2019). The widespread formation of authigenic marine clays has been proposed to be a major sink for Si during the Precambrian due to the absence of pelagic Si-mineralizing organisms (Isson and Planavsky, 2018). Therefore, these shales are prime candidates for in situ Rb-Sr dating to determine their depositional or early marine diagenetic histories. The dominance of cogenetic phases eases laser targeting and provides a good spread in $^{87}\text{Rb}/^{86}\text{Sr}$ ratios. However, high-resolution microscale mineral identification is important for confirming the authigenic mineral dominance and avoiding detrital-phase contamination (see the Supplemental Material).

The abundant clays in the Gibb Member shale UR6_269 are dominantly illite and do not show typical irregular, detrital morphologies, supporting our interpretation of their authigenic origin. Sample UR6_269 is also the only sample to preserve siderite micronodules (Fig. 2A), which are intergrown with an illite and chlorite matrix, suggesting an early-diagenetic origin. This is commonly found in marine shales precipitating under anoxic conditions with high levels of ferrous iron ($\text{Fe}^{2+}$) and limited sulfur (HS⁻) availability (Mozy and Wersin, 1992). The Rb-Sr age of the Gibb Member shale is within its depositional age (Southgate et al., 2000), suggesting that the analyzed bulk-composition illite matrix of this sample formed authigenically during or soon after deposition. Furthermore, the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of this shale (Fig. 3) is within error of estimates for coeval paleo-seawater (Kuznetsov et al., 2014), further confirming the marine origin of the dated assemblage. Although within error, the centroid value is slightly more radiogenic than that of paleo-seawater, which may reflect its shallow-marine or semi-restricted depositional environment (El Meknassi et al., 2020). Nevertheless, we conclude that the geochronology, isotope geochemistry, and petrography of the Gibb Member shale reflect an early-diagenetic signature in equilibrium with contemporaneous ocean water, as opposed to a late-stage nonmarine alteration event.

Bulk XRD data and spectral reflectance analyses of the Derim Derim Dolerite sample UR5_229 (see the Supplemental Material, and Fig. S3; Smith, 2015) indicate its extensive alteration and chloritization. In addition, backscatter electron imaging and elemental mapping of
sample UR5_229 (Fig. S2) reveals many K-rich (and, by inference, Rb-rich) phases. Rb-enriched secondary chlorite is a common product of hydrothermal alteration of mafic protoliths (Duane et al., 2004). The high initial $\frac{\delta^{87}Sr}{\delta^{86}Sr}$ ratio of this sample (Fig. S3) suggests fluid-rock interaction processes involving substantial influx of radiogenic crustal fluids during the purported potassic alteration of the dolerite. The Rb-Sr age obtained from sample UR5_229 dolerite overl laps, within error, the crystallization ages of Derim Derim intrusions obtained elsewhere in the McArthur Basin (Bodorkos et al., 2020; Yang et al., 2020), indicating that this fluid infiltration event likely happened during or soon after dike intrusion.

Energy-dispersive X-ray spectroscopy screening of shales from both the Jalboi Formation and Wooden Duck Member shows evidence for substantial post-depositional alteration (Fig. 2), likely caused by the Derim Derim Dolerite intrusion. Specifically, large chlorite aggregates in the Jalboi Formation replace other earlier clay constituents. In the Wooden Duck Member, illite aggregates display morphologies inconsistent with an early-diagenetic origin, showing fissile and foliated matrices interlocking with quartz overgrowth. In addition, the presence of rutile in these rocks implies secondary redistribution of titanium. Ages and initial $\frac{\delta^{87}Sr}{\delta^{86}Sr}$ ratios from the Jalboi Formation and Wooden Duck Member shales overlap with those from the Derim Derim Dolerite, yielding highly radiogenic and nonmarine values (Fig. 3). Evidence for higher initial $\frac{\delta^{87}Sr}{\delta^{86}Sr}$ ratios in marine carbonates and shales is commonly related to secondary processes such as (1) influence from late-stage diagenetic processes (Phan et al., 2019), (2) the introduction of radiogenic Sr via later diagenetic fluid-rock interactions and metasomatism (Poi trasson et al., 1995), and (3) inputs of radiogenic Sr sourced from detrital grains.

Fluid-rock interaction processes also have significant impact on REE solubility and transport during later alteration. Both shales from well UR5 are depleted in LREEs when normalized to the Gibb Member shale. The Jalboi Formation and Wooden Duck Member shales overlap with those from well UR5_229 (Fig. S2) reveals many K-rich (and, by inference, Rb-rich) phases. Rb-enriched secondary chlorite is a common product of hydrothermal alteration of mafic protoliths (Duane et al., 2004). The high initial $\frac{\delta^{87}Sr}{\delta^{86}Sr}$ ratio of this sample (Fig. S3) suggests fluid-rock interaction processes involving substantial influx of radiogenic crustal fluids during the purported potassic alteration of the dolerite. The Rb-Sr age obtained from sample UR5_229 dolerite overlaps, within error, the crystallization ages of Derim Derim intrusions obtained elsewhere in the McArthur Basin (Bodorkos et al., 2020; Yang et al., 2020), indicating that this fluid infiltration event likely happened during or soon after dike intrusion.

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Fluid-rock interaction processes also have significant impact on REE solubility and transport during later alteration. Both shales from well UR5 are depleted in LREEs when normalized to the Gibb Member shale. The Jalboi Formation shows extreme depletion and has a similar REE pattern to that of the dolerite intrusion (Fig. 3). Multiple factors and processes could have caused the relative LREE depletion observed in these shales. However, the increased LREE depletion with increased proximity of the shales to the intrusion suggests that intrusion-induced hydrothermal alteration is the most likely cause. Physical and chemical buffers have been shown to play a major role in fluid-rock interaction and alteration in marine sediments (Park et al., 2019).

Taken together, the resetting of the Rb-Sr chronometer with highly radiogenic initial $\frac{\delta^{87}Sr}{\delta^{86}Sr}$ ratios, the observed depletions of LREEs, as well as the petrography of the altered shales collected in vicinity of dolerite dike in well UR5 clearly demonstrate that these rocks were altered during or soon after the dolerite emplacement. Previous studies have used the total Fe species measured in shales from well UR5 to infer periods of anoxia during the Proterozoic (Shen et al., 2003). We argue these altered shales may not faithfully record primary paleo–redox conditions because their bulk chemistry has likely been affected by the dolerite intrusion. Consequently, any interpretations made from these rocks to reconstruct past paleoenvironments should be treated with caution.

CONCLUSIONS

We present the first in situ Rb-Sr dating and elemental analyses of Proterozoic illite-rich shales as well as an altered dolerite intrusion. The Gibb Member shale from an intrusion-absent borehole was abundant in authigenic illite and yielded a Rb-Sr age consistent with the depositional age for the unit. In addition, the sample’s initial $\frac{\delta^{87}Sr}{\delta^{86}Sr}$ ratio overlaps with that of ca. 1.5 Ga seawater. In contrast, the Jalboi Formation and Wooden Duck Member shales were sourced from a well containing a dolerite intrusion. We demonstrate that their Rb-Sr isotopic systems were reset by the intrusion and their chemistry has affinities to the altered dolerite. As such, we show that the chronological and geochemical data obtained together by this novel approach can be used to constrain the histories of Precambrian shales effectively where authigenic phases make up the dominant Rb-Sr–bearing constituents.

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