

Sulfur isotope biogeochemistry of the Proterozoic McArthur Basin

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Abstract

Previous geochemical and biomarker studies of the late Paleo-Mesoproterozoic propose a stratified world, with strongly reducing (possibly sulfidic) deep-ocean conditions overlain by an oxygenated surface-ocean and atmosphere. To investigate such a scenario, we look to the structure of the biogeochemical sulfur cycle. We present sulfur (³²S, ³³S, ³⁴S, and ³⁶S in sulfides) isotope data from the McArthur Basin (Barney Creek, Reward, Velkerri, and McMinn formations) that allows for a direct evaluation of the surface biosphere. We are interested in investigating the types of information that can be gained by including ³³S and ³⁶S. When the ³⁴S/³²S fractionations are small, the inclusion of ³³S and ³⁶S provides little additional information, but does provide ancillary evidence for relative isotopic homogeneity (with the internal consistency of ³³S/³²S and ³⁶S/³²S). When the ³⁴S/³²S fractionations are large, direct information about the fractionation mechanisms can be obtained, with the potential to distinguish the biological from abiological processes. For example, the reconstruction of the Roper Group suggests that seawater sulfate concentrations were high enough to buffer against spatial heterogeneities. Overall, our findings agree with previously proposed redox structure of the Proterozoic ocean, highlight contributions from the oxidative sulfur cycle, and outline a new tool for interpreting the state of the surface sulfur cycle.

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1. INTRODUCTION

Detailed isotopic and biological studies of Proterozoic surface environments provide a growing picture of an Earth in transition between an anoxic Archean world and that of the more oxic Phanerozoic (Canfield, 2005; Holland, 2006). The character of the transition from reducing to fully oxygenated includes a proposal that the <2500 million year (Ma) old surface-ocean was oxygen-rich due to active oxygenic photosynthesis (cf. Hayes et al., 1992; Holland, 2006),

whereas the deep-ocean remained anoxic, and likely sulfidic because of the activity of sulfate-reducing microorganisms (SRB: Canfield, 1998; Shen et al., 2002; Arnold et al., 2004; Poulton et al., 2004). Other hypotheses suggest more localized sulfidic conditions (Logan et al., 1995; Shen et al., 2003), including the possibility of trace concentrations of oxygen in deep-water settings (Slack et al., 2007). The redox-stratification of this ocean may have also played a role in biological evolution, as upwelling of anoxic/sulfidic/suboxic waters could have challenged aerobic life, and especially protists, on the continental shelves. The archetype locality for studying the marine biogeochemistry of the late Paleo-Mesoproterozoic is the McArthur Basin, where numerous studies have investigated the sedimentology

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(Crick et al., 1988; Jackson et al., 1988; Abbott and Sweet, 2000; Page et al., 2000), geochemical cycling (Jackson and Raiswell, 1991; Lindsey, 2001; Shen et al., 2002, 2003), paleobiology (Javaux et al., 2001), and organic biomarkers (Summons et al., 1988; Logan et al., 2001; Dutkiewicz et al., 2003; Brocks et al., 2005) of these environments. Thus, we identified the McArthur Basin as an ideal target for the more thorough testing of a new isotopic tool.

Sulfur isotope studies (Canfield and Teske, 1996; Canfield, 1998; Lyons et al., 2000, 2006; Shen et al., 2002, 2003; Kah et al., 2004; Poulton et al., 2004; Gellatly and Lyons, 2005) provide insight into Proterozoic geochemical cycles, as information regarding biological activity and ocean chemistry is preserved in these chemical records. Generally, questions of Precambrian geobiological interest revolve around (1) levels of seawater sulfate [as sulfate may relate to both atmospheric oxygen levels via oxidative weathering and biological activity], (2) pinpointing the presence or absence of different sulfur-utilizing microorganisms [as microbes provide insight into local environmental redox cycling], and (3) the possibility and implications of a long-lived, pervasive sulfidic deep-ocean (related to the overall Earth surface redox state). Researchers have used two different, yet related approaches to understand the evolution of the sulfur cycle and in turn, address some (or all) of these questions. The first approach, similar to that applied here, has focused on the $^{34}\text{S}/^{32}\text{S}$ range observed within a suite of sedimentary sulfides (Cameron, 1982; Strauss and Moore, 1992; Canfield and Teske, 1996; Canfield, 1998, 2004; Canfield et al., 2000, 2007; Shen et al., 2001; Strauss, 2004; Fike et al., 2006). More recently, studies have attempted to construct temporal records using carbonate-associated sulfate (Burdett et al., 1989), a proxy for the isotopic composition contemporaneous seawater sulfate (Burdett et al., 1989; Hurtgen et al., 2002, 2005, 2006; Kah et al., 2004; Lyons et al., 2004; Gellatly and Lyons, 2005; Halverson and Hurtgen, 2007). In either case, detailed geochemical investigations allow constraints to be placed on the character of the surface sulfur cycle and in turn, information can be gained about local/global biogeochemical cycling.

Studies of ^{33}S and ^{36}S in sedimentary sulfides have begun to expand the use of pyrites as paleo-environmental indicators (Johnston et al., 2006). Recent work (Johnston et al., 2006) suggests that the sulfur isotope effects associated with open marine conditions differ from those of restricted environments. The application of this isotope system to paleo-environmental reconstructions may then provide information about both local and global processes, and potentially even help differentiate between the two. However, we do not yet understand the extent to which the inclusion of ^{33}S and ^{36}S data, when placed in tighter $^{34}\text{S}/^{32}\text{S}$ stratigraphic constraints, provides novel and independent information about fractionation mechanisms or the study environment. In this study, we present 51 sulfur (^{32}S , ^{33}S , ^{34}S , and ^{36}S) (and carbon; ^{12}C , ^{13}C) isotope measurements of black shales from two successions of the Proterozoic McArthur Basin. In linking, for the first time, multiple sulfur isotope and carbon isotope chemostratigraphic studies with previous sedimentological and

geochemical constraints, we establish a working framework for investigating the sensitivity of the sulfur isotope system to local, global, and biological change.

2. GEOLOGIC SETTING

The shale samples studied here come from the McArthur Basin, which represents a thick and laterally extensive package of relatively unmetamorphosed and undeformed Proterozoic sedimentary rocks in Northern Australia (Crick et al., 1988; Abbott and Sweet, 2000). The lower division of the McArthur Basin (Nathan and McArthur Groups) hosts world class sedimentary exhalative, or SEDEX mineral deposits (Large et al., 2001; Lyons et al., 2006), in addition to stromatolitic and evaporitic carbonates. The upper division (Roper Group) is dominated by well-sorted quartzarenites and interbedded shales (Jackson et al., 1987; Crick et al., 1988). The generalized stratigraphy is presented in Fig. 1. The extent of the lower McArthur Basin (McArthur Group) is poorly understood, but is thought to have been isolated (or partially restricted) from the open ocean. On the other hand, the sediments of the Roper Group are thought to have accumulated in an epicontinental sea (Jackson et al., 1987), and they represent a distinct depositional environment from the older McArthur Group (Jackson et al., 1987; Abbott and Sweet, 2000; Lindsey, 2001). This apparent contrast in depositional environments, from the likely more restricted McArthur Group to the deeper, more extensive waters of the Roper Group has been (Javaux et al., 2001; Shen et al., 2003) and continues to be ideal for investigating the biogeochemistry of the Proterozoic biosphere.

The McArthur Group has been suggested to represent a restricted, intra-cratonic shallow marine environment (Jackson et al., 1987; Rawlings, 1999), possibly defined by a series of fault-bounded grabens (Crick et al., 1988). Evidence for evaporite cycles, along with lithologic interpretations suggests a general deposition in shallow playas or near shore lagoonal settings (Crick et al., 1988; Rawlings, 1999). However, bedded and locally pyritic carbonaceous siltstone and shale (Pietsch et al., 1991; Bull, 1998) of the Barney Creek Formation (and Caranbirini Formation) are interpreted as recording deeper-water facies of sub-wavebase euxinic origin (Bull, 1998; Rawlings, 1999). In contrast, the overlying Reward Formation is seen as a shallower-water facies deposited under relatively quiet anoxic or euxinic water column conditions (Bull, 1998; Shen et al., 2002). Similarities between the sandstone intervals of the Barney Creek and Reward Formations suggest that the Reward formation (which is rich in carbonate) may represent a shallower water equivalent to the more organic-rich mudstone of the Barney Creek Formation (Bull, 1998). Three U–Pb zircon ages constrain the deposition of the Barney Creek Formation at ~ 1640 Ma (1640 ± 3 Ma, 1639 ± 3 Ma, and 1638 ± 7 Ma; Page and Sweet, 1998). An U–Pb age constraint of 1636 ± 4 Ma for the Lynott Formation (Page et al., 2000), which overlies the Reward Formation, suggests a short depositional period (< 14 Ma) for Barney Creek and Reward sedimentation.

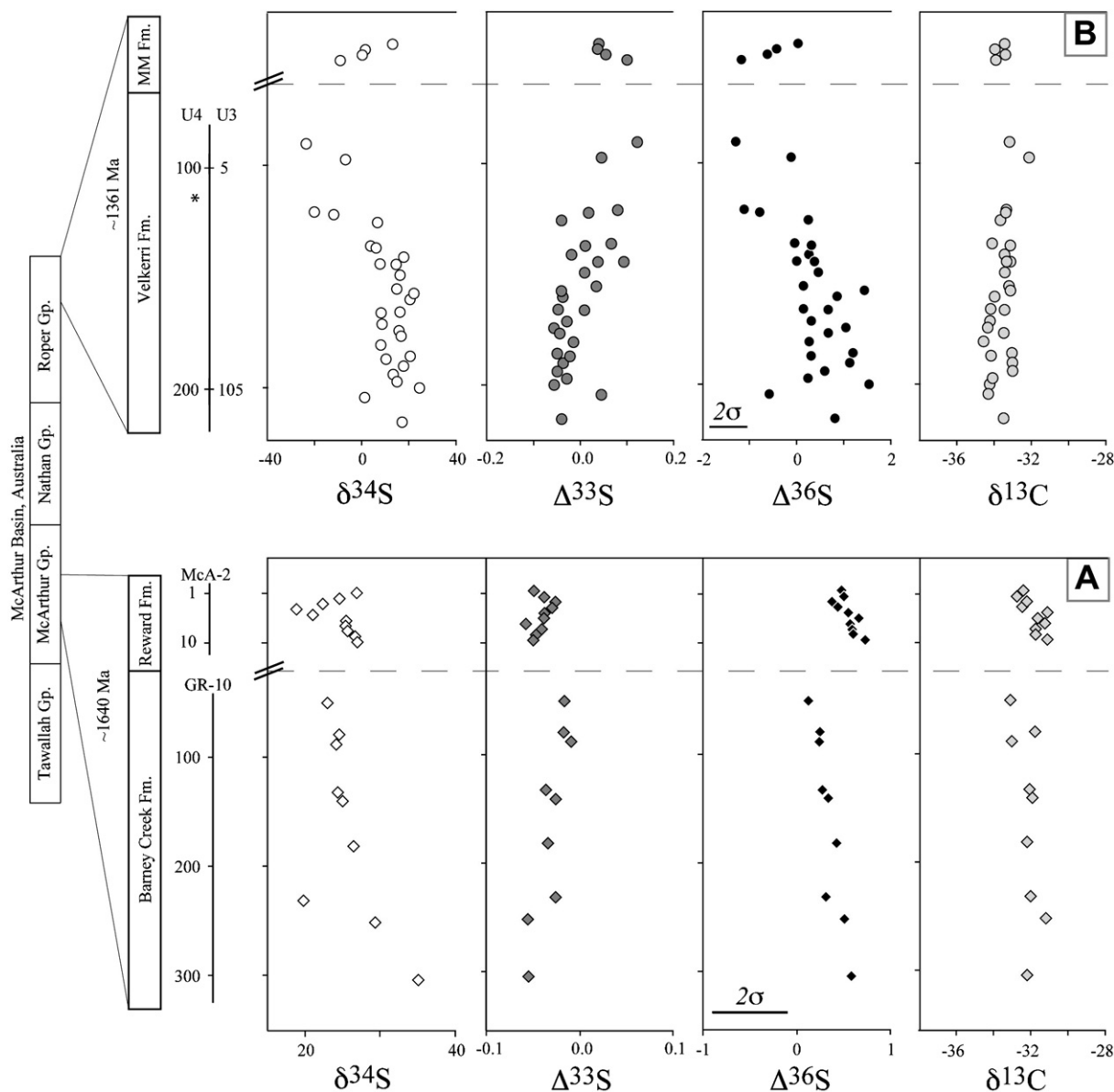


Fig. 1. A chemostratigraphic representation of the isotopic relationships between the McArthur Group (A; lower frame) and Roper Group (B; upper frame), both of which are within the McArthur Basin in present-day northern Australia (modified from Lindsey, 2001). Age constraints are from the Velkerri Formation (noted with * in figure) and Barney Creek Formation. Core information is listed at left, with core material represented for the Barney Creek (GR-10: Glyde River-10), Reward (McA-2: DDH BMR McArthur-2), and Velkerri (U3, U4 :Urapunga 3 and 4, respectively) Formations. McMinn Formation samples are from outcrop. The two Velkerri Formation cores (U3 and U4), as well as samples from the overlying McMinn Formation were matched (in terms of depth and assuming similar rates of deposition) based on the structure of the $\delta^{34}\text{S}$ records. Note the difference in scale between A and B. See Tables 1 and 2 for data. Analytical uncertainties are smaller than the symbols for all but $\Delta^{36}\text{S}$. For $\Delta^{36}\text{S}$, a standard 2σ uncertainty bar is located in the lower left of each column. Carbon isotope data is consistent with previous findings and outlined in Appendix A.

The Roper Group is viewed as a ramp-style shelf setting and is widely accepted as recording transgressive–regressive cycles of coarsening upward sediments, transitioning from coarse sandstone and oolitic ironstones (as is seen in the lower McMinn Formation) into more organic-rich shales (upper McMinn and Velkerri formations) (Abbott and Sweet, 2000). The Velkerri Formation, in particular, is thought to be a low energy, offshore (Abbott and Sweet, 2000), deep-marine environment (Jackson and Raiswell,

1991) dominated by anoxic basinal mudstones (Abbott and Sweet, 2000; Lindsey, 2001) and is interpreted as the deepest water environment within the Roper Group (Lindsey, 2001). Sedimentology and geochemistry of the overlying McMinn Formation suggest a shallow-water, likely inner shelf setting at the base (less than 20 m water depth, Jackson and Raiswell, 1991) with deeper-water (>150 m; Jackson and Raiswell, 1991) represented by overlying shales of the upper McMinn Formation (Crick et al., 1988). A new

Re–Os age constraint on the Velkerri Formation places deposition at $\sim 1361 \pm 21$ Ma (Kendall and Creaser, 2006).

3. NOTATIONS, MODELING, AND METHODS

3.1. Isotopic notation

We report $^{33}\text{S}/^{32}\text{S}$, $^{34}\text{S}/^{32}\text{S}$, $^{36}\text{S}/^{32}\text{S}$ and $^{13}\text{C}/^{12}\text{C}$ data using standard delta notation (δ), where

$$\delta^{33}\text{S} = 1000 \times \left(\frac{^{33}R_{\text{sam}}}{^{33}R_{\text{std}}} - 1 \right), \quad (1)$$

$$\delta^{34}\text{S} = 1000 \times \left(\frac{^{34}R_{\text{sam}}}{^{34}R_{\text{std}}} - 1 \right), \quad (2)$$

$$\delta^{36}\text{S} = 1000 \times \left(\frac{^{36}R_{\text{sam}}}{^{36}R_{\text{std}}} - 1 \right), \quad (3)$$

and

$$\delta^{13}\text{C} = 1000 \times \left(\frac{^{13}R_{\text{sam}}}{^{13}R_{\text{std}}} - 1 \right), \quad (4)$$

and where ‘*sam*’ and ‘*std*’ represent the sample and standard, respectively. The less abundant sulfur isotopes (^{33}S and ^{36}S) are also reported using capital delta notation (Δ), where

$$\Delta^{33}\text{S} = \delta^{33}\text{S} - 1000 \times \left[\left\{ 1 + \frac{\delta^{34}\text{S}}{1000} \right\}^{0.515} - 1 \right] \quad (5)$$

and

$$\Delta^{36}\text{S} = \delta^{36}\text{S} - 1000 \times \left[\left\{ 1 + \frac{\delta^{34}\text{S}}{1000} \right\}^{1.90} - 1 \right]. \quad (6)$$

The exponents in these relationships (0.515 and 1.90) define the reference fractionation line (RFL) and approximate single-step thermodynamic equilibrium isotope exchange effects at low temperature (Hulston and Thode, 1965).

3.2. Geochemical modeling: a review

The modeling associated with this study is an extension of traditional geochemical box models (cf. Garrels and Lerman, 1981) modified to accommodate a multiple isotope system, such as sulfur. Earlier versions of these models are presented in Johnston et al. (2005a) and Johnston et al. (2006). We parameterize the surface sulfur cycle as the interaction between five distinct reservoirs: (1) igneous, or continental sulfur, (2) seawater sulfate, (3) sulfate evaporites or other sulfate deposits, (4) hydrogen sulfide, and (5) pyrite. The interaction between each reservoir is constrained by the relative flux of sulfur between each pool, and any fractionation associated with the transformation. For example, the flux of sulfur from seawater sulfate to hydrogen sulfide is assigned a fractionation factor to account for the process responsible for this transformation (SR: sulfate reduction). Following Canfield and Teske (1996), we assume that the primary source of isotopic fractionation in the sulfur isotope record is microbial, more specifically the effect of SRB and microbial sulfur disproportionation (SDB). To best represent the natural sulfur cy-

cle, the microbial fractionations used in the modeling are taken directly from experimental work with pure and mixed cultures (Farquhar et al., 2003; Johnston et al., 2005b, 2007). This allows for appropriate, empirical constraints to be placed specifically on the ^{33}S and ^{36}S fractionations associated with those microbial reactions.

The product, or output, of this modeling effort is a series of unique predictions for the isotopic composition of each of the surface sulfur cycle reservoirs. For the models presented later in the text, we provide generalized fields that outline the >200 unique model solutions. The isotopic predictions are calculated (and presented) as a function of two flux terms, f_{py} and $f_{\text{r-o}}$. The models are run under steady-state, open system conditions, meaning that these terms represent the relative flux of material. For example, f_{py} represents the relative flux of material leaving the sulfur cycle as pyrite compared to that leaving as sulfate minerals, while $f_{\text{r-o}}$ represents the re-oxidation of hydrogen sulfide to sulfate, relative to the original flux of sulfate to hydrogen sulfide. So, when $f_{\text{py}} = 0$, no sulfur is removed as pyrite (all leaves as sulfate minerals) and when $f_{\text{r-o}} = 0$, no hydrogen sulfide is re-oxidized to sulfate (all exits to pyrite). The processes leading to the re-oxidation of hydrogen sulfide to sulfate are catalyzed by a number of different microbial metabolisms, including SDB. However, other than SDB, most of these processes do not yield large isotopic effects. Thus, we presume that the term $f_{\text{r-o}}$ can be used as a proxy for the presence (not activity) of SDB. As minor isotope data becomes available for other oxidative microbial processes, these can be incorporated into modeling efforts.

We present model predictions for the sulfur cycle that match the natural samples of interest. For instance, Johnston et al. (2005a) presented a model prediction for seawater sulfate and compared this model to measurements of proxies for the seawater sulfate reservoir. In contrast, the samples in this study represent the pyrite fraction of the surface sulfur cycle and are compared to model predictions for the pyrite reservoir. In comparing these model results to natural systems, we add an additional layer of complexity. Rather than using the models to predict global compositions, we are more interested in understanding pyrite compositions in the depositional environment, which may represent a restricted or open marine basin. This modification is accomplished by nesting a sedimentary sub-cycle into the original five-box model (cf. Johnston et al., 2006; Farquhar et al., 2007). Effectively, this simply moves the root of the pyrite model prediction to the composition of seawater sulfate, rather than being pinned at the composition of weathered material (bulk Earth has a composition near zero).

3.3. Chemical methods

Shale samples were crushed and sulfur extracted and precipitated as Ag_2S using techniques outlined in Canfield et al. (1986). Samples from the Reward Formation were previously analyzed (for $\delta^{34}\text{S}$) and presented in Shen et al. (2002). Each Ag_2S precipitate was placed under a 10^{-3} Torr vacuum and fluorinated individually with a $10\times$ excess of F_2 at 250°C for 8 h to produce SF_6 . Sulfur hexafluoride

Table 1
Isotope data for the McArthur Group, McArthur Basin, Australia

McArthur Group Formation	Depth (m)	$\delta^{13}\text{C}$ (‰)	$\delta^{33}\text{S}$ (‰)	$\delta^{34}\text{S}$ (‰)	$\delta^{36}\text{S}$ (‰)	$\Delta^{33}\text{S}$ (‰)	$\Delta^{36}\text{S}$ (‰)	
<i>McA-2</i>								
Reward Fm.	1	−32.41	13.76	26.98	52.35	−0.048	0.47	
Reward Fm.	2	−32.75	12.56	24.60	47.73	−0.037	0.48	**
Reward Fm.	3	−32.22	11.42	22.34	43.24	−0.025	0.37	
Reward Fm.	4	−32.46	9.59	18.75	36.35	−0.028	0.42	
Reward Fm.	5	−31.16	10.73	21.01	40.82	−0.036	0.54	
Reward Fm.	6	−31.64	12.99	25.45	49.35	−0.040	0.45	**
Reward Fm.	7	−31.26	12.93	25.38	49.33	−0.056	0.56	
Reward Fm.	8	−31.81	13.12	25.71	49.99	−0.040	0.57	
Reward Fm.	9	−31.76	13.49	26.44	51.18	−0.036	0.35	**
Reward Fm.	10	−31.13	13.76	26.98	52.41	−0.045	0.53	**
<i>GR-10</i>								
Barney Creek Fm.	51	−33.12	11.74	22.96	44.18	−0.015	0.11	
Barney Creek Fm.	80	−31.79	12.53	24.50	47.30	−0.016	0.23	
Barney Creek Fm.	89	−33.04	12.38	24.19	46.69	−0.008	0.23	
Barney Creek Fm.	133	−32.11	12.45	24.39	47.11	−0.035	0.26	
Barney Creek Fm.	141	−31.95	12.75	24.95	48.27	−0.024	0.32	
Barney Creek Fm.	182	−32.22	13.48	26.40	51.05	−0.033	0.30	**
Barney Creek Fm.	232	−32.02	10.07	19.71	38.08	−0.027	0.30	***
Barney Creek Fm.	252	−31.23	14.98	29.39	57.08	−0.055	0.50	
Barney Creek Fm.	305	−32.24	17.93	35.22	68.54	−0.054	0.57	

Core name is listed above formation name where GR-10: Glyde River-10 and McA-2: DDH BMR McArthur-2. Depths are in meters. Sulfur data are normalized to a V-CDT scale, whereas organic carbon compositions are normalized to V-PDB. Symbols at right (*) represent the number of repeats, with the uncertainties derived from these repeats consistent with, or better than the long-term reproducibility of 0.14‰, 0.008‰ and 0.20‰ for $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$, respectively. Where repeat analyses were performed, average compositions are listed.

(SF_6) was purified cryogenically (distilled at -110°C) and chromatographically (on a 12' molecular sieve 5 Å/Haseq Q column with a TCD). Clean SF_6 was measured as SF_5^+ (m/e of 127, 128, 129, and 131) on a ThermoFinnigan MAT 253 Gas Source Mass Spectrometer. Isotopic data are reported relative to V-CDT, assuming an IAEA S-1 composition of $\delta^{34}\text{S} = -0.36\text{‰}$, $\delta^{33}\text{S} = -0.066\text{‰}$, and $\delta^{36}\text{S} = -1.26\text{‰}$, and with a long-term reproducibility (1σ) of 0.146‰, 0.008‰, and 0.20‰ for $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$. Seven repeat analyses were additionally performed (indicated by * in Table 1) and suggest a reproducibility equivalent to or better than those listed above. Total organic carbon compositions were measured on acidified, decalcified residues by flash combustion at 1030 °C using a Eurovector elemental analyzer inline with a GV Isoprime mass spectrometer. Carbon isotope compositions are normalized to V-PDB and carry an analytical reproducibility of 0.11‰ (1σ) based on multiple analyses of standard materials interspersed with the samples.

4. RESULTS

All isotope data are listed in Tables 1 and 2 and summarized below. The isotopic compositions of samples from the McArthur Group ($n = 19$) have a total range from 35.22‰ to 18.75‰, -0.008‰ to -0.056‰ , and 0.57‰ to 0.11‰ in $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$, respectively (Table 1). The isotopic composition of sulfide samples from the Roper Group ($n = 31$) vary from 24.72‰ to -23.44‰ , 0.125‰ to -0.054‰ , and 1.54‰ to -1.29‰ in $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$, respectively (Table 2). Organic carbon isotope compositions for the McArthur Group vary from -31.13‰ to

-33.12‰ . For the Roper Group, organic carbon values range from -32.11‰ to -34.56‰ (see Appendix A).

Stratigraphic trends for both the McArthur and Roper Groups are presented in Fig. 1. In the McArthur group, the data highlight an up-section decrease of $>15\text{‰}$ in $\delta^{34}\text{S}$, with more punctuated negative excursions within both the Barney Creek and Reward formations. The $\Delta^{33}\text{S}$, $\Delta^{36}\text{S}$ and $\delta^{13}\text{C}$ remain relatively constant throughout. The Roper Group stratigraphic data are marked by $\sim 40\text{‰}$ variability in $\delta^{34}\text{S}$. Records of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ also show variability, with $\Delta^{33}\text{S}$ increasing and $\Delta^{36}\text{S}$ decreasing throughout.

5. DISCUSSION

The target for this study is an improved understanding of the utility of ^{33}S and ^{36}S measurements, and as such we focus on the sulfur records and begin by presenting and interpreting $\delta^{34}\text{S}$ trends. The environmental hypotheses derived from these interpretations are then tested in $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$, both stratigraphically and in triple isotope plots. As the McArthur and Roper groups are separated by >200 Ma, we view each as separate entities and draw conclusions independently.

5.1. The McArthur Group

5.1.1. The chemostratigraphic $\delta^{34}\text{S}$ record

McArthur Group sulfides are notably enriched in ^{34}S when compared to modern sulfides but consistent with previous observations for the McArthur Basin (Shen et al., 2002; Ireland et al., 2004; Lyons et al., 2006). Knowledge that the McArthur Group contains massive exhalative

Table 2
Isotope data for the Roper Group, McArthur Basin, Australia

Roper Group Formation	Depth (m)	$\delta^{13}\text{C}$ (‰)	$\delta^{33}\text{S}$ (‰)	$\delta^{34}\text{S}$ (‰)	$\delta^{36}\text{S}$ (‰)	$\Delta^{33}\text{S}$ (‰)	$\Delta^{36}\text{S}$ (‰)
McMinn Fm.	OC	-33.42	6.87	13.30	25.45	0.043	0.03
McMinn Fm.	OC	-33.94	0.94	1.75	2.91	0.040	-0.42
McMinn Fm.	OC	-33.38	0.28	0.44	0.22	0.058	-0.62
McMinn Fm.	OC	-33.89	-4.50	-8.92	-18.06	0.103	-1.17
<i>Urapunga 3</i>							
Velkerri Fm.	26.6	-33.33	-10.24	-19.95	-38.68	0.083	-1.11
Velkerri Fm.	31.3	-33.65	3.51	6.89	13.39	-0.037	0.25
Velkerri Fm.	41.82	-34.09	2.10	3.95	7.48	0.070	-0.04
Velkerri Fm.	46.86	-33.43	9.23	18.04	34.82	-0.016	0.27
Velkerri Fm.	50.1	-33.11	7.64	14.80	28.70	0.041	0.38
Velkerri Fm.	54.95	-33.42	8.46	16.47	32.00	0.012	0.47
Velkerri Fm.	61.15	-33.19	7.77	15.07	28.98	0.037	0.15
Velkerri Fm.	65.9	-33.96	10.58	20.71	40.58	-0.035	0.86
Velkerri Fm.	71.55	-34.17	8.39	16.43	31.60	-0.044	0.15
Velkerri Fm.	76.98	-34.21	4.51	8.83	17.16	-0.026	0.32
Velkerri Fm.	79.95	-34.33	8.17	16.02	31.71	-0.054	1.05
Velkerri Fm.	82.38	-33.47	8.63	16.92	33.06	-0.041	0.68
Velkerri Fm.	91.41	-33.04	10.61	20.80	41.09	-0.046	1.20
Velkerri Fm.	95.84	-33.01	9.16	17.93	35.48	-0.034	1.13
Velkerri Fm.	99.57	-33.00	6.92	13.57	26.53	-0.046	0.60
Velkerri Fm.	105.6	-34.23	12.60	24.72	49.03	-0.053	1.54
Velkerri Fm.	110	-34.30	0.78	1.42	2.12	0.048	-0.58
Velkerri Fm.	121	-33.48	8.86	17.35	34.04	-0.037	0.82
<i>Urapunga 4</i>							
Velkerri Fm.	90.93	-33.16	-12.02	-23.44	-45.35	0.125	-1.29
Velkerri Fm.	97.97	-32.11	-3.42	-6.73	-12.87	0.049	-0.11
Velkerri Fm.	122.8	-33.36	-6.01	-11.67	-22.84	0.021	-0.78
Velkerri Fm.	137.76	-33.12	3.26	6.31	12.34	0.014	0.32
Velkerri Fm.	145	-33.31	4.19	7.97	15.20	0.097	0.01
Velkerri Fm.	158.17	-33.12	11.41	22.35	44.35	-0.037	1.45
Velkerri Fm.	166.9	-33.43	4.34	8.42	16.74	0.012	0.67
Velkerri Fm.	181.3	-34.56	4.25	8.29	16.08	-0.012	0.27
Velkerri Fm.	187.7	-34.16	5.39	10.53	20.42	-0.019	0.31
Velkerri Fm.	197.8	-34.07	7.78	15.21	29.33	-0.026	0.24

Formations are listed at the left, with core names and depths (in meters) recorded for the Velkerri Formation samples. For the McMinn Formation, 'OC' signifies outcrop. Sulfur data are normalized to a V-CDT scale, whereas organic carbon compositions are normalized to V-PDB. Analytical uncertainties are derived from the long-term reproducibility of IAEA standards, and result in 1 s errors of 0.14‰, 0.008‰, and 0.20‰ for $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$, respectively.

Zn–Pb sulfide deposits aids in our interpretation of the isotopic compositions recorded in these shales. As recently reviewed by Lyons et al. (2006), “McArthur type” deposits are thought to be derived from fluids rich in metals and poor in sulfide, leading to the proposal that most of the requisite sulfur was derived from marine sediments or the overlying water column (if euxinic). Understanding the source of this sulfide is aided by proposals that the Barney Creek and Reward formations were deposited under sulfidic water columns (Shen et al., 2002; Brocks et al., 2005, respectively), further suggesting a syngenetic origin to the sulfide. We use this context to investigate the isotopic systematic and stratigraphic variability within McArthur Group black shales.

The up-section trend in $\delta^{34}\text{S}$ for the Barney Creek Formation shows a systematic decrease from +35‰ to +22‰, with a punctuated negative excursion (down to +19‰) lower in the section (Figs. 1a and 2). Taken out of a stratigraphic context, the simplest explanation of the $\delta^{34}\text{S}$

composition is that the sulfides reflect the quantitative reduction of seawater sulfate. The up-section stratigraphic trend (decreasing $\delta^{34}\text{S}$) fits with one of two possible environmental scenarios. First, the progressive change in compositions may be tracking the evolution of global seawater sulfate. If true, then the decrease in $\delta^{34}\text{S}$ may reflect one of a number of possible changes to the marine sulfur cycle, including but not limited to changes in inputs or outputs (weathering/pyrite burial) to the system.

The isotopic variability might also suggest that this basin experienced some degree of closed system behavior (Rayleigh enrichment). This would allow for an isotopic enrichment in the basin sulfate, and as a result sedimentary sulfide. Following on this interpretation, the stratigraphic interval represented would be capturing the recovery from a more restricted setting (increased sulfate influx). The gradual up-section decrease in $\delta^{34}\text{S}$ values could be explained by increasing communication with a larger, possibly global, sulfate reservoir. This scenario can be

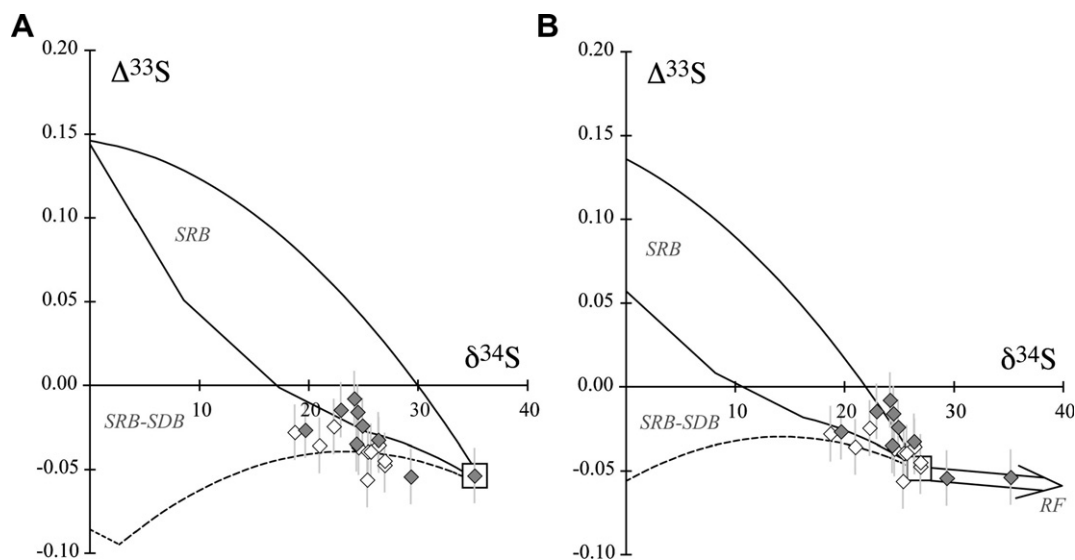


Fig. 2. A plot of $\delta^{34}\text{S}$ versus $\Delta^{33}\text{S}$ for data for the McArthur Group. Also included are model predictions for the composition of sedimentary sulfides. The model solid line encloses compositions that can be described with only SRB, whereas the dashed volume requires SDB. Variability within the model fields is a function of relative pyrite burial (f_{py}) and relative re-oxidation of sulfide ($f_{\text{r-o}}$). Since these are relative fluxes, f values vary from zero to one. Darker diamonds represent the Barney Creek Formation, with lighter diamonds representing the Reward Formation (see Table 1). White squares represent estimates of seawater sulfate. Model details are further described in the text. Uncertainties in $\delta^{34}\text{S}$ are smaller than the symbols whereas $\Delta^{33}\text{S}$ are 2σ . (A) Data from the McArthur Group with a sedimentary sulfide without incorporating conclusions from the $\delta^{34}\text{S}$ chemostratigraphy. (B) Data from the McArthur Group with a sedimentary sulfide with the incorporation of conclusions from the $\delta^{34}\text{S}$ chemostratigraphy, which suggest that the lower Barney Creek Formation experienced a degree of basin restriction/distillation. Also included, and labeled as RF, is a theoretical example of the possible (Rayleigh) distillation effects assuming a typical SRB fractionation.

conceptually understood as two-component mixing where the enriched end-member is the basin sulfate pool (perhaps near $+35\text{‰}$ and a smaller reservoir) and the less enriched end-member would be the larger/global sulfate reservoir (possibly near $+20$, a more common value for global seawater and a larger reservoir). This interpretation would suggest that the composition approached at the top of the Barney Creek Formation might represent, by proxy, the composition of the global sulfate reservoir (or at a minimum the composition of the larger reservoir that the Barney Creek basin is sampling; Shen et al., 2002). The timescale of the recovery would be determined by the rate of water entering the basin (and relative sulfate concentration of both the basin and the larger reservoir) versus the volume of the basin. As these shales reflect a relatively deep facies in an otherwise shallow playa or lacustrine setting, the increased communication may be associated with transgression. The negative excursion at ~ 232 m may reflect a number of transient features, including but not limited to a pulse of weathered continental sulfur, changes in microbial activity, or a sudden decrease in sulfide production.

The $\delta^{34}\text{S}$ of the Reward Formation records much less variability than the Barney Creek Formation. Over the 10 m sampled, $\delta^{34}\text{S}$ values of $\sim +26\text{‰}$ characterize the lower 5 m, followed by a small excursion to $\sim +19\text{‰}$ and recovery back to $+26\text{‰}$ at the top of the sampled section. Interestingly, there appears to be a small range in $\delta^{34}\text{S}$ values shared by the upper Barney Creek Formation and a majority of the sampled Reward Formation (at $\sim +26\text{‰}$). Following on the proposition that the upper Barney Creek

Formation represents an estimate of seawater sulfate (Shen et al., 2002), the similarity of the Reward Formation sulfide compositions (previously interpreted as reflecting quantitative reduction of seawater sulfate; Shen et al., 2002) could be interpreted as suggesting a consistency between seawater sulfate compositions in these depositional environments. Geological observations suggest a potential link between the Reward and Barney Creek formations, with the Reward Formation representing the shallow-water equivalent to the Barney Creek Formation.

5.1.2. Triple isotope relationships of the McArthur Group

The primary goal of this part of the study is to test the utility of measurements of $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ and to further expose what types of information, if present, these records preserve. Of special importance are those interpretations related to stratigraphic variability. The primary interpretation of the McArthur Group, based on $\delta^{34}\text{S}$ evidence, is that the isotopic composition of basinal/global seawater evolved during deposition of the Barney Creek Formation. Overall, the isotopic variability observed in the McArthur Group shales is small (Fig. 3), with isotopic compositions clustering with slightly negative $\Delta^{33}\text{S}$ (and positive $\Delta^{36}\text{S}$). Within this general grouping, a majority of the data (17 of 19) are even more tightly clustered, with the two outliers representing the lowermost Barney Creek Formation samples. This observation is also consistent with the distribution of samples in $\delta^{34}\text{S}$ versus $\Delta^{36}\text{S}$. Given this observation, two simple interpretations are possible: the first calls on normal marine conditions whereas the alterna-

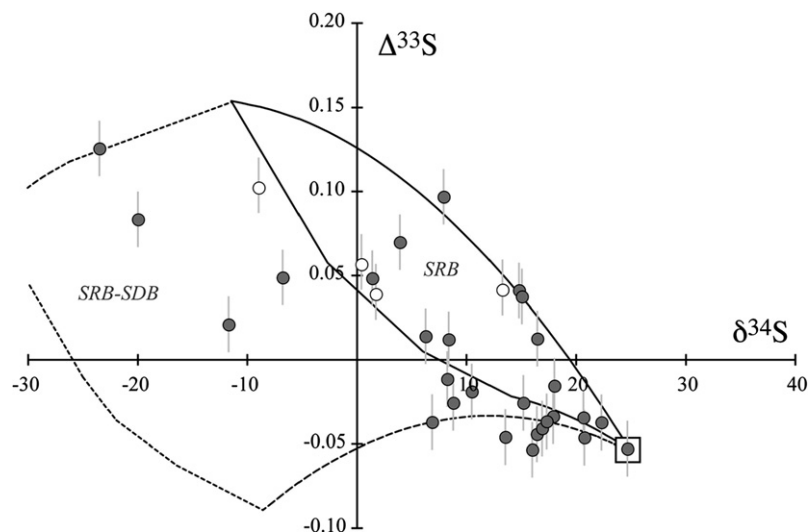


Fig. 3. A plot of $\delta^{34}\text{S}$ versus $\Delta^{33}\text{S}$ for data for the Roper Group. Included are model predictions for the composition of sedimentary sulfides, where solid line encloses compositions that can be described with only SRB whereas the dashed volume requires SDB. Variability within the model fields is a function of relative pyrite burial (f_{py}) and relative re-oxidation of sulfide ($f_{\text{r-o}}$). Darker circles represent the Velkerri Formation, with white circles representing the McMinn Formation (see Table 2). The white square represents an estimate of seawater sulfate. Model details are further described in the text. Uncertainties in $\delta^{34}\text{S}$ are smaller than the symbols whereas $\Delta^{33}\text{S}$ are 2σ .

tive interpretation considers the isotopic consequence of basin restriction.

Differentiating between possible interpretations can be accomplished through comparison with isotope model predictions, the details of which are outlined in Section 3.2. As the models represent steady-state, open system behavior, the first information gained through this treatment is the open or closed nature of the environment being evaluated. Simply, if the model can explain the variability observed in the data, then the environment is seemingly behaving in an open and steady-state fashion (where the size and composition of the marine sulfur cycle is largely unchanged). Closed system behavior (where the size and composition of the marine sulfur cycle can evolve) also carries specific isotopic consequences that can be diagnosed independent of the models used to describe open system behavior (see Johnston et al., 2006 for a discussion). As the overall $\delta^{34}\text{S}$ variability is small, differentiating between the possible scenarios (open and closed) is difficult.

When the sulfide model is applied to the McArthur Group samples, all of the measured compositions can be satisfied (within 2σ , Fig. 2a). This implies that, if the system was behaving as an open system, the composition of the sulfate from which the sulfide formed had a composition of $\delta^{34}\text{S} \geq +35$, $\Delta^{33}\text{S} \leq -0.05$ (and $\Delta^{36}\text{S} \geq +0.50\text{‰}$). This sulfate would represent either pore-water or bottom-water sulfate (white box in Fig. 2). This is a lower compositional limit, as sulfate with greater $\delta^{34}\text{S}$ ($\Delta^{36}\text{S}$) and more negative $\Delta^{33}\text{S}$ could also satisfy the data. Using this framework, the steady-state model field is sub-divided into a region where both SR and SD (sulfur disproportionation) are considered to be active, and a second field where only SR is required to produce the observed compositions. Since the variability is minimal, it would be misleading to draw major conclusions about the presence or absence of SDB; however, this gen-

eral interpretation would point to high values of f_{py} , suggesting a steady and near quantitative conversion of sulfate to sulfide.

Earlier, we discussed the possibility that the depositional environment of the Barney Creek Formation experienced partial closed system behavior, and the record presented in Fig. 1a ($\delta^{34}\text{S}$) may reflect the increased communication with a larger (global) sulfate pool. This scenario would require the isotopic enrichment of basin sulfate be lower in the section than is measured here, with the sampled portion of the stratigraphy recording the recovery from such an event, rather than the direct distillation itself. As noted above, this scenario requires a fine balance between water exchange rates and basin volume. If true, it would be expected that the $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values that accompany samples with $\delta^{34}\text{S} \sim +26\text{‰}$, or inferred global seawater value, would then also represent the global seawater composition. As demonstrated in Fig. 1a, at depths (in the cores) where the $\delta^{34}\text{S}$ is $\sim +26\text{‰}$, consistent $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ are also recorded ($\Delta^{33}\text{S} \sim -0.02$ and $\Delta^{36}\text{S} \sim +0.25\text{‰}$). Thus, the second interpretation of the McArthur Group suggests that the basin sulfate pool, which had undergone a degree of distillation to acquire a $\delta^{34}\text{S}$ of $+35\text{‰}$, is slowly incorporating sulfate from an external, possibly global sulfate reservoir. In this scenario, the global reservoir would have a general composition of roughly $\delta^{34}\text{S} \sim +25\text{‰}$, $\Delta^{33}\text{S} \sim -0.05\text{‰}$, and $\Delta^{36}\text{S} \sim +0.50\text{‰}$, which is the composition approached at the top of the sampled Barney Creek section and recorded in a majority of the Reward Formation samples. If correct, it would be expected that the general composition of the outlying samples from the lowermost Barney Creek Formation could be achieved by Rayleigh distillation. Solving $R_0 = R_f \times F^{(\alpha-1)}$ for each isotope (where R is a ratio, F is the fraction of sulfate remaining and α is a fractionation factor: Johnston et al., 2006), suggests that

distillation by SR (with a typical SR fractionation¹) would drive sulfate towards the compositions measured from the lowermost Barney Creek Formation. Unfortunately, as the range of measured $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values is small, the inclusion of these data does not significantly improve our understanding of the McArthur Group depositional environment.

5.2. The Roper Group

5.2.1. The chemostratigraphic record

Sulfur isotopic data for the younger Roper Group (drill cores Urupunga 3 and 4 [U3 and U4], outcrop from the McMinn) are presented in Figs. 1b and 3. Previous interpretations (Logan et al., 1995; Shen et al., 2003) of $\delta^{34}\text{S}$ data from U4 and other cores through the Roper Group suggested that more isotopically depleted samples ($\delta^{34}\text{S} < 0$) reflect basinal settings with limited reduction of seawater sulfate (observed in the upper portion of the section: Fig. 1b), whereas heavy $\delta^{34}\text{S}$ sulfides reflect the quantitative reduction of seawater sulfate, likely in a shallower water environment ($\delta^{34}\text{S} > 10\text{‰}$) (observed in the lower portion of the section: Fig. 1b). The previously discussed relationship between $\delta^{34}\text{S}$ and water depth (Shen et al., 2003) is based on sequence stratigraphy (Page et al., 2000) and is supported by a fossil study of the Roper Group (Javaux et al., 2001). As discussed in Shen et al. (2003), the up-section trend in Fig. 1b could then be interpreted as recording the transition from shallow to deep-water settings, with the overlying McMinn Formation recording a shallowing (or regressive) event. In keeping with Shen et al. (2003), the $\delta^{34}\text{S}$ measured in the lower Velkerri Formation is thought to reflect the isotopic composition of the overlying seawater sulfate ($\delta^{34}\text{S} \sim 25\text{‰}$). Also included in the Shen et al. (2003) study, iron speciation data from the Roper Group suggests that the deeper, basinal sediments were deposited under a sulfidic water column.

5.2.2. Triple isotope relationships of the Roper Group

We observe a much larger range of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ variability in the Roper Group than the McArthur Group sulfides, with a resolvable and monotonic increase in $\Delta^{33}\text{S}$ inversely correlated to $\Delta^{36}\text{S}$ (Fig. 1b). The greater $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ variability (when compared to the McArthur Group) is due to a wider $\delta^{34}\text{S}$ range, which is a result of the mass-dependent nature of these systems (see Ono et al., 2006 and Farquhar et al., 2007). The correlation between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$, which in this case is quite strong, is thought to reflect the dominant microbial process in the basin (SR). The samples from the Roper Group systematically collapse toward a single $\delta^{34}\text{S}$ – $\Delta^{33}\text{S}$ composition as $\delta^{34}\text{S}$ increases and $\Delta^{33}\text{S}$ decreases (Fig. 3, lower right). This is a prescriptive characteristic because the shape of the field de-

finied by the data is very similar to that predicted from our models. Applying a similar approach as above, we note that the sulfide model field can satisfy all the data (Fig. 3), meaning that with one choice of local sulfate (square in figure), an open system, steady-state model prediction can describe all of the measured compositions. Our first conclusion is then that the Roper Group sulfides do not contain explicit evidence for any local distillation effects. Considering that the Roper Group is thought to be a shelf/ramp setting and that the sulfate pool is stable, the prospect of the overlying water column reflecting global seawater is even more realistic. More importantly, however, the wide scatter recorded in the Roper Group samples allows for a better test of whether both SRB and SDB are active in the basin, or whether just SRB are present. The data fall within both sub-fields (see Fig. 3) suggesting that the isotopic effects recorded in these shales represent the combined influence of both SRB and SDB.

In contrast to the McArthur Group, ^{33}S and ^{36}S data lend strong support and expand upon conclusions derived from $\delta^{34}\text{S}$. The striking consistency between the field defined by the scatter in the data and the shape of our models predictions makes a strong case for the appropriateness of these models. These data suggest that the Roper Group is behaving in a fashion representative of a larger marine setting, likely in communication with the open ocean. Further, the isotopic signals from these sulfides carry definitive evidence for active oxidative sulfur cycle (SD). The isotopic variability could be the result of variable contributions from oxidative processes, changes in relative sulfate reduction rates (and nutrient availability), or iron availability (as it pertains to pyrite formation).

5.3. The co-variation of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$

Next we quantify the relationship between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ (or $\delta^{33}\text{S}$, $\delta^{34}\text{S}$, and $\delta^{36}\text{S}$). There is an expectation for the co-variation of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ that is based on the relative mass difference between the more trace isotopes (^{33}S and ^{36}S) and the reference isotope (^{32}S ; see Farquhar and Wing, 2005; Johnston et al., 2006; Ono et al., 2006 for further discussion), a relationship most commonly conveyed as a slope ~ -7 array. Using established regression methods (Johnston et al., 2006), the McArthur Group data suggest a $\Delta^{33}\text{S}$ versus $\Delta^{36}\text{S}$ slope of: $\Delta^{36}\text{S} = -8.3 (\pm 1.4) \Delta^{33}\text{S} + 0.11 (\pm 0.05)$. The array extending through the Roper Group data suggest a $\Delta^{33}\text{S}$ versus $\Delta^{36}\text{S}$ slope of: $\Delta^{36}\text{S} = -11.4 (\pm 1.5) \Delta^{33}\text{S} + 0.32 (\pm 0.08)$. The entire data set follows $\Delta^{33}\text{S}$ versus $\Delta^{36}\text{S}$ trends (Fig. 4) similar to that of other Proterozoic marine environments (Johnston et al., 2006, in press).

In addition to data from the McArthur Basin, three arrays are included in Fig. 5 for reference. The first is a generalized relationship for non-mass-dependent fractionations (NMD), the second approximates a theorized mass-dependent fractionation (MD), and the third characterizes the process of sulfate reduction (SR). Note that, despite different arrays, both MD and SRB represent completely mass-dependent processes. NMD effects characterize the Archean and earliest Paleoproterozoic sedimentary record,

¹ Using Rayleigh fractionation equations and fractionation factors of $^{33}\alpha = 0.9897$, $^{34}\alpha = 0.9800$, and $^{36}\alpha = 0.9619$, the most enriched $\delta^{34}\text{S}$ (and corresponding $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values) can be satisfied with 40% sulfate drawdown. These fractionations are near averages for microbial sulfate reduction published in Johnston et al. (2007).

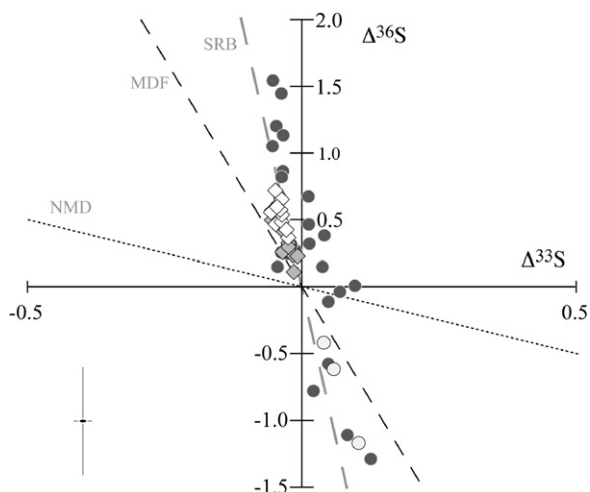


Fig. 4. The relationship between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$. Also included is a representative 2σ error bar, and the characteristic mass-dependent (MDF) and non-mass-dependent (NMD) lines of slope -6.85 (Ono et al., 2006) and -1 (Farquhar et al., 2000), respectively. The third line included for reference represents the SRB relationship from (Johnston et al., 2007). Barney Creek Formation samples are represented by gray diamonds, Reward Formation samples by white diamonds, dark circles are from the Velkerri Formation, and light circles are from the McMinn Formation.

whereas the remainder of Earth's history (including the Proterozoic McArthur Basin) is dominated by MD effects. The theoretical line (MD) is an estimate of low temperature inorganic reactions (see Farquhar and Wing (2003); Johnston et al., 2007). As is demonstrated, the relationship between the data and mass-dependent predictions (MD and SRB) is a much better match than with the NMD average. This observation suggests that these samples (and by proxy, depositional environments) received no significant isotopic contributions from weathered Archean terrain carrying appreciable NMD sulfur (Farquhar et al., 2000, 2007). The close match between these data and the SRB array is suggestive, supporting the view that these microorganisms dominated the sulfur cycle at this time. The presence and activity of SDB would shift this value towards greater values (~ -6 ; see Johnston et al., in press). This is not to argue SR was the only active microbial process (as our data suggests the activity of SD), but does point to the prominence of this metabolism.

6. CONCLUSIONS

In this study, we present the first stratigraphic interpretation of the total, mass-dependent sulfur isotope system. We tested the utility of ^{33}S and ^{36}S in providing additional information to that gained from the traditional $\delta^{34}\text{S}$ measure. Using sediments from the archetype middle Proterozoic environment, the McArthur Basin (Northern Australia), this study focused on the older, and likely more restricted McArthur Group and the younger, likely more open marine Roper Group. Sulfides samples from the McArthur Group span a limited range in $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$. As a result, a definitive environmental conclusion

was illusive and the added data simply reinforced the isotopic consistency seen in $\delta^{34}\text{S}$. Conversely, the Roper Group data cover a wide range in $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$. In interpreting these additional relationships, the Roper is seen as representing a stable marine system. The isotopic variability observed within the Roper Group data does not appear to be the relic of basin dynamics (as was the case for the McArthur), but in fact due to spatial gradients and specific depositional environments (water depth). Future work should be directed at further investigating these environmental gradients.

As the Roper Group is thought to reflect an open marine system, it can be used as a proxy for a more global marine condition, even though geologic evidence suggests a possible epicontinental setting. An intriguing aspect of our interpretation suggests that the entire suite of sulfides sampled from the Roper Group (especially the Velkerri Formation, where the sample density is greater) may have been formed in a marine setting with a homogeneous sulfate reservoir. This conclusion is reached on the grounds that a single seawater sulfate isotopic composition (and models thereafter) can account for the entire range of fractionations observed, suggesting an apparent isotopic heterogeneity. This suggests that sulfate concentrations were high enough to buffer against spatial heterogeneities.

As the body of ^{33}S and ^{36}S data grows, these records will also shed light on the longer-term evolution of the surface sulfur cycle. A provocative recent study (Canfield, 2004) suggested that the bulk composition of the Earth's surface sulfur reservoir might have changed throughout the Proterozoic, aiding in our ability to account for extreme compositions in the terminal Proterozoic. The inclusion of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ will undoubtedly allow for further constraints to be placed on the processes active within the sulfur cycle, and may contribute to our understanding of the mechanisms (be they biological or tectonic) responsible for any potential change in the composition of the surface sulfur reservoir.

Our data also provide a better understanding of Proterozoic microbial activity, as sulfides from the Mesoproterozoic Roper Group show strong evidence of active microbial disproportionation. Though recent work suggests a more ancient onset of SDB (Kaufman et al., 2007; Philippot et al., 2007), our results reinforce the presence and activity of oxidative cycling in the middle Proterozoic. As the environmental requirement for active SDB is the presence of sulfur intermediate species (S^0 , SO_3 , S_2O_3), which are generally understood to be the product of microbial sulfide oxidation (either phototropic or non-phototropic utilizing O_2 or NO_3), other microbial and geochemical processes must have also been present. With geochemical evidence for sulfidic water column conditions (Jackson and Raiswell, 1991; Shen et al., 2003) and biomarker evidence for active purple and green sulfur bacteria in the McArthur Basin (Brocks et al., 2005), it is easy to see how the sulfur intermediate species required to fuel SD were present when these sediments were deposited. Perhaps it was the establishment of ocean stratification (circa 1800 Ma: Poulton et al., 2004) and the sudden availability of hydrogen sulfide in the photic zone that allowed for widespread SDB activity. As future

work further unravels the history of oceanic chemical change, the story of microbial evolution will follow.

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APPENDIX A. THE CARBON ISOTOPE RECORD

The remarkable stability of the organic carbon isotope record through both the McArthur and Roper groups (and that of inorganic carbonate in equivalent strata) provides information about both the late Paleo-Mesoproterozoic carbon cycle and Proterozoic biogeochemistry. In the context of previous work, isotopic stasis in carbonate (Strauss and Moore, 1992; Buick et al., 1995; Knoll et al., 1995; Kah et al., 2001) and organic carbon (Des Marais et al., 1992; Des Marais, 1997, 2001) is a defining characteristic of this time, thus not a surprising feature these shales. This observation has led to inferences about the stable balance between oxidized and reduced oceanic species throughout this interval (Buick et al., 1995), which by analogy can be extrapolated to constant levels of atmospheric molecular oxygen and carbon dioxide, as well as possibly marine sulfate. An alternative interpretation relies on the possibility of a large, standing marine pool of dissolved organic carbon (DOC) (Rothman et al., 2003).

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