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Redox-sensitive metals and $\delta^{238}\text{U}$ in red and grey shales:

Exploring a new archive for palaeo-redox studies

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Abstract

Reconstructions of past oceanic redox conditions, based on the measurement of metal distributions and their stable-isotope ratios in marine sediments, have now become more commonplace, providing new constraints on past environmental change. Almost all of these records, however, are based on organic-rich black-shale and carbonate sedimentary archives, which have formed primarily in low-latitude regions. This limitation leads to incomplete geographic coverage that complicates the global-scale interpretation of the results. In this study, the potential of oceanic ‘red beds’ and grey shales as new archives of past environmental conditions are explored to complement the datasets derived from other lithologies and extend reconstruction efforts to mid- to high-latitude regions. Our records originate from open-marine red and grey shales from two sedimentary sections spanning the Late Cretaceous Oceanic Anoxic Event 2 (OAE 2) in New Zealand, formerly deposited at high southern latitudes in the palaeo-Pacific Ocean at c. 94 Ma and where contemporaneous black-shale and/or carbonate successions do not exist. Access to the seawater-derived, authigenic fraction of the bulk sediment is essential for reconstructing past marine redox state at these mid- to high-latitude locations. Therefore, a series of leaching experiments using reagents of progressively increasing concentration were conducted to determine the best method for isolating the authigenic Fe- and Mn-(oxyhydr)oxide fraction from the red and grey shale lithologies. Chemostratigraphic records for the concentrations of a suite of redox-sensitive metals (Fe, Mn, Co, Ni, Mo, Cr, V and U), as well as the U-isotope palaeo-redox tracer ($^{238}\text{U}/^{235}\text{U}$; reformulated as $\delta^{238}\text{U}$), were obtained. These records imply that leaching with 6 M HCl at room temperature is the best of the tested methods for the selective extraction of the Fe- and Mn-(oxyhydr)oxide phase, whilst minimising the contribution from older inherited detrital material that potentially could confound the interpretation of the chemostratigraphic records. This method offers

potential for reliably constraining the authigenic distributions of redox-sensitive elements in red and grey shales, provided Fe- and Mn-(oxyhydr)oxides are predominantly of authigenic origin and constitute at least 5 % of the mineralogy. By contrast, for the investigation of the U-isotope system, a larger Fe- and Mn-(oxyhydr)oxide proportion in the sediment for an ocean–atmosphere perturbation event recording more severe changes in ocean redox conditions and bigger U-isotope shifts than observed for OAE 2 are both necessary to obtain reliable results.

KEYWORDS:

Oxyhydroxides, shales, leaching, trace metals, uranium isotopes, OAE 2, paleoredox

MAIN TEXT:

1 Introduction

Reconstruction of the evolution and stabilisation of past environmental conditions following climate-related perturbations, including the oxygenation status of former oceans, is crucial to understanding modern and future oceanic deoxygenation in response to global warming and its impact on marine life. The tracing of past oceanic redox conditions is traditionally based on distributions of redox-sensitive metals in marine sediments (e.g., Tribovillard et al., 2006; Little et al., 2015; Sweere et al., 2016; Yano et al., 2020) and has more recently been complemented by the systematics of their metal stable-isotope systems, which offer the potential to provide more detailed insights into past oceanic changes. For example, the generally long oceanic residence times of molybdenum (Mo) and uranium (U) makes their respective ^{98}Mo - ^{95}Mo and ^{238}U - ^{235}U redox-sensitive isotope systems ideal for tracing the global evolution of ocean oxygenation (e.g., Kendall et al., 2015; Dickson et al., 2016; Clarkson et al., 2018; Siebert et al., 2021). Taken together, these metallic element systems have provided important new constraints on past environmental changes during the Great Oxidation Event (GOE) of the early Proterozoic, representing the initial rise of atmospheric oxygen on Earth (c. 2.3 billion years ago [Ga]; e.g., Chi Fru et al., 2016; Gumsley et al., 2017; Greaney et al., 2020), the Oceanic Anoxic Events (OAEs) of the Mesozoic Era (c. 183–85 million years ago [Ma]), the largest and most severe of which was OAE 2 (c. 94 Ma; e.g., Jenkyns, 2010; Clarkson et al., 2018; Sweere et al., 2020), and the warm hyperthermals of the early Cenozoic Era (c. 58–44 Ma; e.g. Dickson et al., 2012; Clarkson et al., 2021).

In sedimentary archives, the metallic elements and their isotopes are preserved in two key sedimentary phases, namely (i) the authigenic fraction, derived from mineral assemblages formed by precipitation and/or adsorption reactions in seawater and marine sedimentary

porewater, such as carbonates, iron (Fe)- and manganese (Mn)-(oxyhydr)oxides, organic matter and sulphides, and (ii) the detrital fraction, comprising generally older, inherited terrestrial mineral assemblages from weathered continental crust, such as aluminosilicate and quartz grains, which enter the oceans as the suspended load primarily via rivers. The authigenic fraction provides direct information on the chemical state of the oceans at the time of mineral formation, and successful isolation of this fraction provides highly sought-after temporal records of oceanic changes during major environmental re-organisations and perturbations.

To date, the most widely investigated sedimentary archive for reconstructing past ocean-atmosphere perturbations is organic-rich black shale. In these sediments, the metallic elements are typically extracted using whole-rock digestion procedures due to large authigenic enrichments in the organic phases, such that the detrital component contributes relatively little to the bulk sediment trace-metal budget (e.g., Leventhal, 1991; Lipinski et al., 2003; Cruse and Lyons, 2004). Correction for the minor detrital influence is then usually undertaken by normalising the elements of interest to the content of a detrital element, typically aluminium (Al) or alternatively zirconium (Zr), titanium (Ti) or thorium (Th) (Calvert and Pedersen, 1993; Tribovillard et al., 2006). This approach assumes that the detrital trace element resides almost exclusively in detrital rather than authigenic material. The detrital correction has been found to be sufficiently robust when the detrital contribution is comparatively small and at the 5–20 % level (Kryc et al., 2003; Tribovillard et al., 2006).

However, in black shales from certain depositional settings, such as near-shore environments that are strongly influenced by continental erosion and riverine runoff, or where organic-matter production and preservation rates are comparatively low, a substantial detrital component can be present in the whole-rock digests. This contribution can dominate the metallic element signatures of the bulk sediments, leading to unreliable elemental

concentrations being derived for the marine-based authigenic fraction, even after normalisation using Al as a detrital tracer. In this case, it may be preferable to selectively leach the authigenic fraction by partial digestion, leaving the majority of detrital minerals behind in the undigested residue (e.g., Yang et al., 2004; Xu et al., 2012; Gangl et al., 2023). This process is typically achieved using aqua regia (3:1 molar ratio of HCl:HNO₃) or inverse aqua regia (1:2 molar ratio of HCl:HNO₃) digestion procedures, both of which dissolve authigenic carbonates, Fe- and Mn-(oxyhydr)oxides, organic matter and sulphides, while at the same time minimising the dissolution of inherited detrital silicate minerals.

Although widely recognised as providing highly valuable information on past ocean–atmosphere conditions in relation to global climate change, archives constituted by organic-rich black shales have two key limitations. First, black shales, which form under anoxic or euxinic (anoxic and sulphidic) conditions, may be either perturbed by local redox conditions, or located in restricted basins, both of which potentially obscure global signatures. This drawback is particularly problematic for global redox tracers, notably the U- and Mo-isotope systems (Andersen et al., 2014, 2017; Gangl et al., 2023). Second, the deposition of organic-rich black shales is under-represented at mid- to high latitudes, as shown on the example of black-shale coverage during OAE 2 (Fig. 1a; Wang et al., 2011). Incomplete geographical coverage of organic-rich black shales has hindered the reconstruction of past climatic conditions on a global scale, biasing reconstructions towards lower latitude sites in the northern hemisphere, especially for records based on local or regional environmental proxies.

An alternative, yet under-explored sedimentary archive for palaeoceanographic conditions is given by Fe- and Mn-(oxyhydr)oxides. These minerals are formed in seawater and marine sedimentary porewater and have been shown to record the global U-isotope composition of the oceans, albeit likely with an isotopic offset (Goto et al., 2014; Wang et al., 2016).

Previous studies have focussed on extraction of the authigenic Fe- and Mn-(oxyhydr)oxide phase from marine ferromanganese nodules and crusts in order to reconstruct palaeoceanographic conditions on million-year timescales or longer (e.g., Reynolds et al., 1999; Frank et al., 2002; Wang et al., 2016). In these formations, Fe- and Mn-(oxyhydr)oxides comprise the dominant mineral phase and the majority of the bulk sample. However, slow-growing ferromanganese nodules and crusts are not suitable for reconstruction of past oceanic redox events that occur on shorter, 100 thousand-year (ky) timescales because they lack sufficient temporal resolution (Mizell and Hein, 2018). Alternative archives offering higher resolution records of palaeoceanographic change, but with diffuse and smaller proportions of Fe- and Mn-(oxyhydr)oxides, remain under-explored.

An unconventional sedimentary archive that forms with sufficiently fast growth rates to record multi-millennial-scale oceanic redox changes and where the authigenic phase comprises Fe- and Mn-(oxyhydr)oxides is given by ‘oceanic red beds’, which formed globally at mid- to high latitudes, as well as in low-latitude regions (Wang et al., 2009). Therefore, chemostratigraphic information from marine red-bed sedimentary sections has the potential to complement black-shale records, allowing reconstruction of a more complete picture of the spatial and temporal extent of palaeoceanographic changes during past carbon-cycle perturbations. Oceanic red beds are typically deposited either during climate recovery episodes following environmental degradation and oceanic anoxic conditions (Hu et al., 2006; Scott et al., 2009) or under generally more oxygenated settings. As an example, Fig. 1b shows the global coverage of oceanic red beds at 80 Ma (Wang et al., 2011) after OAE 2, highlighting the extended geographical coverage afforded by this archive.

Despite their potential significance in palaeoenvironmental reconstruction, to date only a very limited number of elemental concentration datasets and metal-isotope records are

available for oceanic red beds, none of which are specifically targeted at the Fe- and Mn-(oxyhydr)oxide fraction (Robinson et al., 2009; Hu et al., 2012; Perri et al., 2013; Khorassani et al., 2015; Luan et al., 2021). The palaeoenvironmental reconstruction necessary for Fe- and Mn-(oxyhydr)oxide minerals mostly represent only a minor component of the total rock mass (<1 %) in this underutilised sedimentary archive (Hu et al., 2009), making their reliable extraction exceedingly challenging. In this context, regardless of the chemical procedure used to preferentially extract these minerals, it is likely that, for at least some of the metallic elements, the sedimentary concentrations and isotopic signatures will represent a combination of the detrital and authigenic phases, rather than being dominated by the authigenic signature alone. It is therefore imperative to use a selective extraction technique with chemicals of sufficient purity to minimise metallic element contamination that both minimises the detrital proportion in the leachate and maximises the selective extraction of the Fe- and Mn-(oxyhydr)oxide fraction.

In this study, we have, for the first time, attempted to develop a selective leaching procedure suitable for trace-metal studies, to reliably extract the Fe- and Mn-(oxyhydr)oxide component of both oceanic grey shales and an oceanic red bed consisting of red shales. In this manner, we extend the potential of the authigenic Fe- and Mn-(oxyhydr)oxide component of both oceanic red and grey shales as a new archive of past environmental conditions to complement the datasets derived from other more established lithologies. We have conducted a series of acid-leaching experiments on sediments from two well-characterised OAE 2 sections and assessed the ability of each method to reliably extract redox-sensitive metal concentrations. We also aimed to evaluate the performance of each method for extracting the compositions of the Mo- and U-isotope global-ocean redox tracers in red and grey shales. Molybdenum content is, however, low in these sections, allowing only the U-isotopic system to be assessed. The best-performing method for Fe- and Mn-(oxyhydr)oxide extraction was then applied to the full

stratigraphies of the investigated OAE 2 sections to further assess the viability of oceanic red and grey shales for direct reconstruction of ocean redox-conditions. Whilst vast areas of the oceans were anoxic during OAE 2, the extent to which ocean de-oxygenation persisted in the south-west Pacific region during OAE 2 remains under-constrained due to a lack of local carbonate and/or black shale archives from which reconstructions of ocean redox state are conventionally derived. The red and grey shales of Mangaotane B and Sawpit Gully in New Zealand provide a unique opportunity to help address this knowledge gap.

2 Materials and methods

2.1 Sedimentary sections

Red and grey shale samples from two Cretaceous sites in New Zealand (Mangaotane B on the eastern North Island and Sawpit Gully on the north-eastern South Island; Fig. 1c and Fig. 1d) were investigated in order to develop an optimal method for the selective extraction of the Fe- and Mn-(oxyhydr)oxide phase from the bulk sediment. Both sites have well-exposed and well-characterised sections spanning OAE 2 of Cenomanian–Turonian age (Crampton et al., 2001 and references therein; Hikuroa et al., 2009; Hasegawa et al., 2013). These OAE 2 strata were deposited at a palaeolatitude of approximately 65–70°S (Sutherland, 1999; Strogon et al., 2023) along the eastern continental margin of the proto-New Zealand landmass at about the time of its separation from the Gondwana supercontinent. Samples from both locations have previously been investigated, in high resolution, for their magnetic susceptibility (MS), total organic carbon content (TOC) and organic $^{13}\text{C}/^{12}\text{C}$ (presented in per mil relative to Vienna Pee Dee Belemnite as $\delta^{13}\text{C}_{\text{TOC}}$; Gangl et al., 2019). For both locations, the stratigraphy shows a broad positive carbon-isotope excursion (CIE) marking the timing and duration of OAE 2 and

illustrates many of the characteristic features of the event (e.g., Tsikos et al., 2004), especially in the stratigraphically expanded Sawpit Gully section. Both sequences are highly bioturbated and mottled to varying degrees, which indicates the presence of oxygen during and shortly after deposition, an interpretation corroborated by generally low amounts of TOC.

While both sites consist of grey mudstone to very fine sandstone, Mangaotane B also has a ~16 m thick major red bed, at stratigraphic heights of 28.6–44.6 m, that spans the entire second half of the stratigraphic expression of OAE 2 (Fig. 2a). These red shales have previously been identified as Cretaceous Oceanic Red Beds (CORBs) deposited under oxic conditions (Hikuroa et al., 2009). The red coloration is attributed to the presence of hematite (Fe_2O_3), which is believed to have developed diagenetically shortly after sediment deposition from hydroxide species formed in oxidising environments and therefore carrying the primary seawater signature of redox-sensitive metals (e.g., Eren and Kadir, 1999; Hu et al., 2005; Hikuroa et al., 2009). The environment of deposition for Mangaotane B was likely to have been at upper slope depths of ~300 m or greater (Crampton et al., 2001). The depositional onset of the major red bed in Mangaotane B coincides with an abrupt rise in MS and a sudden drop in wt % TOC, 50 cm below the change in lithology, which has been interpreted as a dramatic change in weathering regime and/or intensity (Gangl et al., 2019).

The Sawpit Gully section consists of grey mudstone to very fine sandstone (Fig. 2b) whose depositional environment is poorly constrained, but the lithology and stratigraphic context suggest mid- to outer shelf depths (Crampton, 2023). Total organic carbon and MS levels are relatively invariant in Sawpit Gully with the exception of two prominent maxima, halfway through the OAE 2 interval.

2.2 Sample selection

High-resolution C-isotope (in $\delta^{13}\text{C}_{\text{TOC}}$) stratigraphies for Mangaotane B and Sawpit Gully (Gangl et al., 2019) delineate (i) a period of relative stability before the onset of OAE 2 and its associated environmental degradation ('pre-OAE 2'), followed by the OAE 2 proper characterised by (ii) a relatively sharp initial increase commonly taken to define the onset of the OAE and an augmentation in global carbon burial, followed by (iii) a 'trough', which is the result of a temporary return to cooler, more oxygenated conditions, widely referred to as the 'Plenus Cold Event' (PCE) (Gale and Christensen, 1996; Pogge von Strandmann et al., 2013; Jenkyns et al., 2017; Clarkson et al., 2018; Gangl et al., 2019; O'Connor et al., 2020), as well as a gradual decrease in $\delta^{13}\text{C}_{\text{TOC}}$ likely representing a reduction in global carbon drawdown ('early OAE 2'), followed by (iv) a relatively stable plateau phase denoting renewed intense carbon removal ('late OAE 2'), and finally (v) a gradual decrease in carbon sequestration and $\delta^{13}\text{C}_{\text{TOC}}$ back to pre-excursion values (Gangl et al., 2019) (Fig. 2).

In this study of redox-sensitive metals, one sample representative of each of the 'pre-OAE 2', 'early OAE 2' at the onset of the PCE, and 'late OAE 2' intervals, as identified from their C-isotope stratigraphies, was selected from each OAE 2 location to evaluate the performance of six different digestion methods of progressively increasing reagent strength to selectively leach the Fe- and Mn-(oxyhydr)oxide phase from sediments (Fig. 2). Due to the anomalously low $\delta^{13}\text{C}_{\text{TOC}}$ in Mangaotane B, the plateau phase could not be unambiguously identified and therefore the 'late OAE 2' sample was selected from the beginning of the final phase of the CIE where $\delta^{13}\text{C}_{\text{TOC}}$ was decreasing. The best-performing selective digestion method that optimises release of the Fe- and Mn-(oxyhydr)oxide phase was then applied to an additional 43 samples from Mangaotane B and 15 samples from Sawpit Gully. All samples were analysed for their trace-metal concentrations and U-isotopic composition to further assess

the ability of red and grey shales to record fluctuations in local and global ocean redox conditions throughout the development of OAE 2.

2.3 Sample preparation

All sample preparation methods and analytical protocols were performed in the Centre for Trace Element Analysis, University of Otago. The 58 selected samples were oven-dried at 40 °C for at least 12 h before obtaining pristine sample fragments from the interior of each sediment block using a Dremel drill fitted with a diamond-coated blade. The sample fragments were powdered in an agate mortar and pestle under clean conditions, and approximately 0.5–10.0 g of powdered material was sub-sampled for subsequent digestion, measurement of elemental concentrations, and U-isotope analysis.

2.4 Digestion protocols

The five chemical extraction methods used to selectively extract the Fe- and Mn-(oxyhydr)oxide phase from the bulk sediment and the whole-rock digestion approach are summarised below.

(1) Room temperature (RT) 1 M HCl digestion expected to extract the carbonate and Fe- and Mn-(oxyhydr)oxide phases (Raiswell et al., 1994): Approximately 2 g of rock powder was leached in 20 mL of 1 M HCl. Extractions were carried out on an orbital shaker for 40 h at room temperature.

(2) RT 6 M HCl digestion expected to extract the carbonate and Fe- and Mn-(oxyhydr)oxide phases (Leventhal and Taylor, 1990): Approximately 2 g of rock powder was leached in 20 mL of 6 M HCl. Extractions were carried out on an orbital shaker for 30 h at room temperature.

(3) Hot 6 M HCl digestion expected to extract the carbonate and Fe- and Mn-(oxyhydr)oxide phases (modified from Leventhal and Taylor, 1990): Approximately 2 g of rock powder was leached in 20 mL of 6 M HCl. Extractions were carried out on a hotplate held at 120°C for 30 min.

(4) Hot 10 M HCl digestion expected to extract the carbonate and Fe- and Mn-(oxyhydr)oxide phases (modified from Raiswell et al., 1994): Approximately 2 g of rock powder was leached in 20 mL of 10 M HCl. Extractions were carried out on a hotplate held at 120°C for 30 min.

(5) Aqua regia (3:1 molar ratio of HCl:HNO₃) digestion expected to extract carbonates, Fe- and Mn-(oxyhydr)oxides, organic matter and sulphides (Xu et al., 2012): Approximately 2 g of rock powder was initially digested with ~16.5 mL of 10 M HCl for 30 min, then admixed with an additional 3.5 mL of concentrated 15 M HNO₃ to give a total volume of 20 mL, and digested on a hotplate held at 120°C for 3 h.

(6) Whole-rock total digestion: Approximately 1 g of rock powder was sequentially digested to completion using concentrated 28 M HF, 7 M HNO₃, and 6 M HCl on a hotplate held at 120°C for 5 days.

Extractions with hydroxylamine hydrochloride and sodium dithionite have been suggested previously for the selective extraction of the Fe- and Mn-(oxyhydr)oxide phase (Kunze, 1965; Chester and Hughes, 1967; Gibbs, 1973). However, these reagents are not available in an ultrapure form and would introduce significant contamination to many of the elements of interest, and therefore were deemed unsuitable for this study.

289

290 2.5 *Elemental concentration analysis*

291 Concentrations of redox-sensitive elements (Fe, Mn, cobalt [Co], nickel [Ni], chromium
292 [Cr], vanadium [V], U, Mo), detrital elements (Al, Th, Ti, Zr), and rare earth elements (REE)
293 for monitoring (lanthanum [La], cerium [Ce], praseodymium [Pr], neodymium [Nd], samarium
294 [Sm], europium [Eu], gadolinium [Gd], dysprosium [Dy], holmium [Ho], erbium [Er], thulium
295 [Tm], ytterbium [Yb] and lutetium [Lu]) were measured by quadrupole ICP-MS with 7500cs
296 and 7900 instruments (Agilent Technologies, USA) using external calibration methods and a
297 suite of SI-traceable ICP-MS concentration standards. A multi-element internal standard was
298 admixed to every sample in order to correct for instrumental fluctuations. Analytical precision
299 was verified by repeat measurement of samples and analytical accuracy was verified by the
300 analysis of the certified reference materials BHVO-2 (Hawaiian Volcanic Observatory Basalt;
301 United States Geological Survey (USGS), USA) and BCR-2 (Columbia River Basalt; USGS,
302 USA). Errors for elemental concentrations are given as two times the combined standard
303 deviation (2 SD), taking into account all sources of uncertainty, and are typically <10 % for
304 elements with concentrations above the instrumental limit of detection.

305

306 2.6 *Uranium-isotopic analysis*

307 An aliquot corresponding to 80 ng of U was removed from each digest for U-isotope
308 analysis and then chemically processed using protocols modified from previous methods
309 (Stirling et al., 2007; Murphy et al., 2014; Rolison et al., 2017; Clarkson et al., 2018). A ^{236}U -
310 ^{233}U double spike was added to each sub-sample to obtain a $^{236}\text{U}/^{235}\text{U}$ of ~ 3 , in order to correct
311 for instrumental mass fractionation during analysis, before U separation and purification by

ion-exchange chromatography using UTEVA® resin (Eichrom Technologies, USA). $^{238}\text{U}/^{235}\text{U}$ ratios were measured by MC-ICPMS using a Nu Plasma HR instrument (Ametek Ltd, USA). The U-isotope data are presented in standard δ -notation in ‰ relative to the ‘zero-delta’ CRM-145 U-isotope standard (National Institute of Standards and Technology, USA) that was analysed using the same analytical conditions on either side of each sample analysis according to equation (1). Uncertainties are stated as two times the standard error (2 SE) and account for the internal errors of the sample and bracketing standard measurements, combined in quadrature using standard error propagation techniques. The typical 2 SE value is ± 0.08 ‰, which is comparable to the long-term 2 SD external precision.

$$\delta^{238}\text{U}_{\text{samp}}(\text{‰}) = \left(\frac{\left(\frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{samp}}}{\left(\frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{CRM-145}}} - 1 \right) \cdot 1000 \quad (1)$$

3 Results

3.1 Elemental concentrations in the test leachates

The elemental concentrations of all partial and total digestions are given in Table 1. The relative proportion of each element extracted using the five different acid-leaching methods relative to its total concentration in the bulk sample are shown in Fig. 3.

The percentages of detrital elements (Al, Th, Ti and Zr) extracted during all partial digestions are generally low, but increase as reagent strength increases and range from <1 % to 10 % in the diluted acid (RT 1 M HCl), 1–22 % in the intermediate-concentration acids (RT

6 M HCl, and hot 6 M HCl) and 1–36 % in the higher concentration acids (hot 10 M HCl and aqua regia) for all detrital elements.

The percentages of redox-sensitive elements extracted during partial digestion also increases with increasing acid concentrations, although the overall proportions are lower in the Sawpit Gully extracts than in the Mangaotane B leachates. Partial digestion with RT 1 M HCl leached up to 63 % of the trace-metal inventory, including the release of up to 44 % of Fe and 50 % of Mn, while <10 % of the detrital elements were released in parallel. The extractions with RT 6 M HCl, hot 6 M HCl and hot 10 M HCl all released similar proportions of most redox-sensitive elements, with relatively high percentages of Mn (61–88 %), Fe (48–74 %), Co (54–80 %) and Ni (51–84 %) being extracted, all of which are strongly associated with Fe- and Mn-(oxyhydr)oxides, while 1–22 % of the detrital elements were extracted in the same leachates. Extractions with aqua regia released marginally higher amounts of most elements compared to the HCl extractions. The trace metals were extracted in proportions varying from 6–100 % in the aqua regia digests, including the release of up to 95 % of Mn and 92 % of Fe, while between 3 % and 36 % of the detrital elements were released in parallel.

The chemical index of alteration (CIA) describing the proportion of Al_2O_3 relative to labile oxides and the degree of weathering was calculated for all whole-rock digests following equation (2). Values for CIA of 0.5–0.65 were obtained for both sampling sites (Fig. 4).

$$CIA = \frac{Al_2O_3}{CaO + Na_2O + K_2O + Al_2O_3} \quad (2)$$

3.2 *Uranium-isotope ratios in the test leachates*

The $\delta^{238}\text{U}$ signatures of the test leachates range from $-0.41 \pm 0.07 \text{ ‰}$ to $-0.14 \pm 0.09 \text{ ‰}$ (Fig. 5, Table 2). U-isotope ratios of all leachates agree, within error, with those of the total digest of the same sample, irrespective of which of the six digestion protocols was employed. For the Sawpit Gully leachates, $\delta^{238}\text{U}$ signatures of the different extraction methods are relatively invariant and can be described by 2 SD values that are comparable to the analytical uncertainty of $\sim 0.08 \text{ ‰}$ (Fig. 5). By contrast, $\delta^{238}\text{U}$ values of the leachates for Mangaotane B show some resolvable variations (Fig. 5), with a 2 SD of $\sim 0.15 \text{ ‰}$ for all three samples, which is two-fold larger than the analytical uncertainty. This result indicates that some additional U-isotope fractionation process/es are recorded by the Mangaotane B partial digests.

4 **Discussion**

4.1 *The detrital background of the Mangaotane B and Sawpit Gully sections*

Whole-rock digests from the Mangaotane B and Sawpit Gully sections are dominated by detrital mineral assemblages. Aluminium is widely used as a detrital tracer (Calvert and Pedersen, 1993; Tribovillard et al., 2006) due to its large quantities in terrestrial aluminosilicate minerals, combined with its relative biogeochemical inertness in the marine environment. Therefore, all elemental concentrations were normalised to Al to correct for variations in detrital sedimentation, assuming that all Al is inherited from detrital sources. The whole-rock digests from Mangaotane B and Sawpit Gully have similar elemental compositions after Al-normalisation (Fig. 4), which reflect their similar lithological characteristics.

Although selective for the non-detrital fraction, leachates acquired using strong acids including HCl and aqua regia can attack certain silicates (e.g. Raiswell et al., 1994; Snäll and Liljefors, 2000). Consequently, a small proportion of the elements in the partial leachates could be derived from the detrital fraction. This effect is particularly prominent for sediments deposited on the continental shelf or slope, such as the red and grey shales of the OAE 2 sediments at Mangaotane B and Sawpit Gully. These sediments may have been strongly influenced by erosion and riverine runoff and hence contain a substantial and highly variable detrital component, and Fe- and Mn-(oxyhydr)oxides may be present only at sub-percent levels in such sedimentary deposits (Shaw and Weaver, 1965). The Fe and Mn concentrations of the whole-rock digests of the OAE 2 sediments (3–4 % and 0.03–0.07 %, respectively) confirm that Fe- and Mn-(oxyhydr)oxides comprise only a very minor (<5 %) component of the bulk sediment (Table 1). The increasing percentages of leached Al, and of the other detrital elements, Th, Ti and Zr (Fig. 3), suggests that the proportion of detrital material released during partial digestion increases with progressively intensifying reagent strength. Therefore, a detrital correction needs to be applied to the leachate metal concentration results. Such a correction can be achieved by normalisation using a detrital tracer, combined with the elemental composition of the detrital end-member, which enables the elemental composition of the non-detrital fraction to be characterised.

Typically, average upper continental crust (UCC; Rudnick and Gao, 2014) is used as the detrital end-member. This end-member composition is sufficiently robust when the detrital correction is relatively small. However, many elements in the investigated New Zealand bulk sediments are depleted compared to UCC, therefore, instead of UCC, a *de facto* detrital end-member is needed to carry out a reliable detrital correction on the investigated sections where the detrital contribution is sizeable. The basement rocks underlying Eastern Zealandia are composed of the Torlesse and Waipapa Composite Terranes, which are dominated by sandstone

and argillite that accumulated close to, and were accreted to, the Eastern Gondwana subduction margin during the Permian to latest Early Cretaceous (MacKinnon, 1983; Sutherland, 1999; Mortimer et al., 2014). Beneath the North Island, these rocks extend from the axial ranges eastwards to the modern plate boundary at the Hikurangi subduction margin. Beneath the north-eastern South Island, they underlie all areas from the Alpine Fault eastwards to the subduction margin (Fig. 1d). The Torlesse Composite Terrane (hereafter referred to as ‘Torlesse’) (Hines, 2018) best represents the primary sediment source to both sections and provides a more suitable detrital end-member when correcting for the detrital contribution to the inventories of the leached elements. While Co and Mo concentrations are not available for the Torlesse to enable a direct comparison, most other elements in the Mangaotane B and Sawpit Gully whole-rock digests show concentrations that are generally comparable to those of the Torlesse (Price et al., 2015), reinforcing its suitability as the local detrital end-member lithology. Of note is the fact that most of the Sawpit Gully whole-rock digests show slight depletions in Mn compared to the Torlesse and very low Mo concentrations that are generally below the instrumental limit of detection. This geochemical pattern is likely the result of Mn and Mo loss during weathering, supported by the CIA index that indicates weak weathering at both sites (Fig. 4) (Tang et al., 2018).

4.2 *The best method to extract the Fe- and Mn-(oxyhydr)oxide phase from red and grey shales*

Importantly, a substantial proportion of both Fe and Mn is leached during each of the partial digestions using intermediate- and higher concentration acids, ranging from 53–68 % for the RT 6 M HCl leaching procedure to 64–95 % for the aqua regia digest (Fig. 3). This result compares favourably with the relatively small proportions of detrital elements released

for the same extractions of 1–18 % to 3–36 % for the RT 6 M HCl and aqua regia protocols, respectively. The preferential dissolution of Fe and Mn is also apparent when plotted against released Al content, where leached concentrations of both Fe and Mn plot significantly higher than their bulk compositions and the Torlesse detrital end-member (Fig. 6). Taken together, these observations indicate that the majority of released Mn and Fe is associated with Fe- and Mn-(oxyhydr)oxide minerals rather than detrital silicate material. This geochemical partitioning is because (oxyhydr)oxides are the only non-detrital phase harbouring significant amounts of Fe and Mn in the Mangaotane B and Sawpit Gully sections, as the other possible host phases, namely carbonates for Mn and sulphides for Fe, are negligible in these New Zealand sediments (cf. Calvert and Pedersen, 1996; Raiswell and Canfield, 1998; Xu et al., 2012; Gangl et al., 2019). Low levels of Fe sulphides are also confirmed by the comparable levels of Fe released with HCl and aqua regia, indicating that the majority of Fe is associated with (oxyhydr)oxides, as only aqua regia is able to attack the sulphide phase.

Some elements, including Co, Ni and Mo, are strongly adsorbed onto Fe- and/or Mn-(oxyhydr)oxides (Bertine and Turekian, 1973; Murray and Brewer, 1977). A substantial proportion of both Co and Ni of up to 90 % is leached during each of the partial digestions (Fig. 3), with Co and Ni concentrations showing enrichments relative to detrital Al, and correlating significantly with Fe and Mn release, following the compositions of their respective bulk samples (Fig. 6 and Fig. 7). This correlation is a strong indication that the vast majority of the Co and Ni inventories reside in the Fe- and Mn-(oxyhydr)oxide phase, which is gradually dissolved with progressively intensifying reagent strength. The leached proportions of Mo in the partial digestions are much smaller than those of Co and Ni, and Mo content is below the instrumental limit of detection for many leachates, especially those from Sawpit Gully (Fig. 3). Partial leachates with quantifiable Mo concentrations show its enrichment relative to Al, plotting above their corresponding bulk compositions (Fig. 6). This distribution suggests that

Mo mostly resides in the non-detrital fraction and is progressively released during leaching, as expected. However, relative to Fe and Mn, the leachates plot below their respective bulk compositions (Fig. 7). Such a geochemical pattern indicates a depletion of Mo in the Fe- and Mn-(oxyhydr)oxide phase, most probably caused by loss during weathering, as suggested by the CIA values (Greaney et al., 2021). Taken together, the high proportions of Fe, Mn and elements strongly adsorbing onto Fe- and/or Mn-(oxyhydr)oxides in the partial leachates confirms the selective dissolution of the Fe- and Mn-(oxyhydr)oxide fraction, and all HCl-based leaching procedures are considered suitable for releasing this fraction from red and grey shales.

The selective dissolution of other redox-sensitive elements (Cr, V and U) from the very minor Fe- and Mn-(oxyhydr)oxide fraction of red and grey shales is exceedingly challenging. These elements are only moderately adsorbed onto Fe- and Mn-(oxyhydr)oxides (Langmuir, 1978; Wehrli and Stumm, 1989; Peterson et al., 1997) and the proportions released during partial leaching of up to 37 % are appreciably smaller than the release of Fe and Mn and elements strongly adsorbed onto Fe- and/or Mn-(oxyhydr)oxides of up to 96 % (Fig. 3). While Cr and V in the partial leachates are enriched relative to detrital Al and plot above the composition of their respective bulk samples (Fig. 6), their correlated release with Fe and Mn dissolution lies below the composition of the bulk samples, indicating they are depleted in the Fe- and Mn-(oxyhydr)oxide phase (Fig. 7). As both Cr and V are insoluble to moderately soluble (Rudnick and Gao, 2014), it is unlikely that these elements are being mainly released from the detrital fraction. Instead, Cr and V might be leached from an authigenic phase other than Fe- and Mn-(oxyhydr)oxides, such as authigenic clay minerals that are known to adsorb Cr (Peterson et al., 1997).

Contrary to the other redox-sensitive elements, U is generally not enriched relative to detrital Al in the partial leachates. Also, U dissolution is in general not strongly correlated with Fe and Mn release, and the U-Fe-Mn systematics show that the Fe- and Mn-(oxyhydr)oxide fraction is depleted in U (Fig. 7), implying that this phase is not the primary host of authigenic U in the investigated New Zealand sedimentary sections. For all partial digests of the late OAE 2 red shale from Mangaotane B, the released U approximately co-varies with released Al, plotting along the Torlesse detrital end-member (Fig. 6). This relationship suggests that leached U may primarily be derived from the detrital fraction and that the authigenic phase is devoid of U in the major red bed unit of Mangaotane B. By contrast, released U is depleted relative to Al content in the partial leachates of the other grey shale samples of Mangaotane B and Sawpit Gully and plots below the composition of the bulk sample. Assuming that Al is a reliable detrital tracer for the New Zealand sections, this depletion suggests that the leached U is derived from very specific mineral assemblages within the detrital phase, and/or another authigenic phase in addition to Fe- and Mn-(oxyhydr)oxides, all containing less U than the bulk detrital phase.

Although U concentrations alone were insufficient to determine the host phase from which leached U originates, the application of U-isotopes may be able to shed light on identifying the host phase. In addition, U isotopes in various leachates of the same sample can be used to evaluate the extent to which the leaching procedure itself generates U-isotope fractionation as an analytical artefact.

4.3 Correction for detrital contributions to elemental concentrations and U isotopes in the Mangaotane B and Sawpit Gully stratigraphies

The Fe, Mn, Co, Ni, Cr and V inventories all show enrichments relative to detrital Al content. However, the leaching patterns of all investigated detrital elements (Al, Th, Ti and Zr) suggest that some detrital material has been released during partial digestion and a correction for this detrital contribution needs to be carried out. While the detrital contribution to each of the redox-sensitive elements is expected to be adequately represented by the Torlesse, the choice of the ideal detrital tracer is more complex.

The detrital tracers Ti and Zr mainly reside in accessory minerals, such as zircon, ilmenite and rutile, and are not representative of the main detrital phase (Dellwig et al., 2000; Nesse W D, 2004). Thorium and Al can be adsorbed onto metal oxides, allowing for their presence in small quantities within the Fe- and Mn-(oxyhydr)oxide phase (Kryc et al., 2003; Roy-Barman et al., 2009), which is indicated by Al/Ti enrichment in all partial leachates (Fig. S1). Consequently, Al in the leachates is likely derived from a mixture of detrital and authigenic sources and is expected to over-correct for the detrital contribution, whereas Ti is anticipated to under-correct for it.

Therefore, detrital corrections to derive the authigenic concentrations of Fe, Mn, Ni, Cr and V have been carried out using both, Al and Ti as detrital tracers, following equations (3) and (4). The concentration of element X corrected for the detrital contribution is given as X_{corr} , where $X/\text{Al}_{\text{Torlesse}}$ is the X/Al ratio of the Torlesse detrital end-member, $X/\text{Ti}_{\text{Torlesse}}$ is the X/Ti ratio of the Torlesse detrital end-member (Price et al., 2015) and X_{meas} , Al_{meas} and Ti_{meas} are the measured concentrations of element X, Al and Ti in the sample. As Co concentrations are not available for the Torlesse, a detrital correction could not be carried out for this element. The uncertainties of X_{corr} were calculated using standard error propagation techniques.

$$X_{corr} = X_{meas} - \frac{X}{Al_{Torlesse}} \cdot Al_{meas} \quad (3)$$

$$X_{corr} = X_{meas} - \frac{X}{Ti_{Torlesse}} \cdot Ti_{meas} \quad (4)$$

The corrected elemental concentrations in leachates with 1 M HCl are systematically lower than in the other partial digests (Fig. 8, Table S1). Accepting that all HCl-based digestion procedures attack the Fe- and Mn-(oxyhydr)oxide fraction, these data indicate that 1 M HCl does not quantitatively dissolve the (oxyhydr)oxide phase in the New Zealand sediments. Both grey shale samples from Mangaotane B show uniform Al-corrected authigenic Fe, Mn, Ni and Cr concentrations in all other partial leachates, which confirm that the applied detrital correction method using the Torlesse as the detrital end-member effectively corrects for the leached detrital phase in these samples. By contrast, correction using Ti does not result in uniform Cr concentrations. However, almost all grey shale samples from Sawpit Gully have diverging X_{corr} concentrations in partial digestions using aqua regia compared to the other leaching methods, which is also the case for V_{corr} in grey shale samples from Mangaotane B, irrespective of the detrital tracer used. Given this ambiguity, the aqua regia digestion method is not considered to be reliable for the isolated extraction of the (oxyhydr)oxide phase. In contrast to the grey shale samples, X_{corr} concentrations show more scatter across the range of different leaching methods in the red shale sample of Mangaotane B, irrespective of the detrital tracer used. However, most elements, including Fe and Mn, express uniform X_{corr} concentrations in the RT 6 M HCl, hot 6 M HCl and hot 10 M HCl leachates, once more confirming the effectiveness of these leaching methods.

Despite the assumed over-correction (Al-normalisation) and under-correction (Ti-normalisation) of the detrital contribution in the partial leachates, both detrital tracers lead to similar uniformity of authigenic element concentrations. In the interest of consistency with the

detrital correction of the whole-rock digests, Al has been chosen for the detrital correction of the full stratigraphies of both OAE 2 sites.

As discussed previously, the leached inventories of U are not clearly associated with the minor authigenic Fe- and Mn-(oxyhydr)oxide phase and may instead be largely affiliated with the detrital fraction. Consequently, effective correction for the detrital contribution may be problematic and is discussed in detail in the Supplementary Material. In brief, calculations using Th as a detrital tracer seem to reliably correct for the detrital contribution to U in partial leachates of the grey shale samples from Mangaotane B. However, detrital-corrected U concentrations in these samples may be derived from multiple authigenic phases and $\delta^{238}\text{U}_{\text{corr}}$ data indicate that the leaching method with RT 6 M HCl is the best of the tested methods to extract the Fe- and Mn-(oxyhydr)oxide fraction. Attempts to calculate authigenic signals in Mangaotane B red shales and grey shales from Sawpit Gully yielded spurious results and neither U_{corr} nor $\delta^{238}\text{U}_{\text{corr}}$ in these samples are considered to reliably represent seawater signatures.

Given the likelihood of Mo loss during weathering leading to sedimentary depletions, with Mo concentrations commonly below the instrumental limit of detection, no further attempt was made to extract Mo-isotope signatures from the test leachates.

In summary, partial digestion with RT 6 M HCl is the best of the tested methods for all investigated elements in both sediment types, grey and red shales. However, while red shales from Mangaotane B and grey shales from Sawpit Gully express reliable results for most elemental concentrations, U concentrations and U-isotope ratios give spurious results and are therefore deemed unreliable in reconstructing palaeo-ocean signatures.

4.4 *Authigenic versus secondary Fe- and Mn-(oxyhydr)oxides in grey and red shales at Mangaotane B and Sawpit Gully*

Iron- and Mn-(oxyhydr)oxides are assumed to be the primary authigenic phase in the grey and red shales at Mangaotane B and Sawpit Gully and the partial leaching procedures with HCl have shown to selectively attack these minerals. However, none of the New Zealand samples show enrichment in whole-rock compositions of either Fe or Mn compared to the detrital background represented by the Torlesse (Fig. 4). Consequently, there is the possibility that the Fe- and Mn-(oxyhydr)oxides are not purely authigenic in origin but could have in part been formed on land prior to sedimentary deposition and transported to the depositional site together with detrital particles (Bayon et al., 2004).

Proxies that have been used to shed light on the origin of Fe- and Mn-(oxyhydr)oxides are given by the REE (e.g. Bayon et al., 2004; Yang et al., 2024). Seawater-like REE distributions in (oxyhydr)oxides are typically characterised by an enrichment in heavy REE compared to light REE and by a positive Ce anomaly (Bau et al., 2014). None of the partial digestions of the New Zealand samples express this pattern (Fig. S6, Table S2). While diagenetic modifications during reductive dissolution of Fe- and Mn-(oxyhydr)oxides could be a possible explanation for the depletion in heavy REE relative to light REE (Elderfield and Sholkovitz, 1987), diagenesis is expected to lead to a negative Ce anomaly (Bau et al., 2014).

In any case, the original pattern of REE adsorbed to authigenic Fe- and Mn-(oxyhydr)oxides in the south Pacific Ocean during OAE 2 is not known and deconvolving the origin of the leached Fe- and Mn-(oxyhydr)oxide phase exceeds the scope of this study. However, differences in the REE patterns of the partial leachates compared to the whole-rock digests once more confirms the selective dissolution of the non-detrital fraction. To further assess whether the minor authigenic (oxyhydr)oxide phase of red and grey shales can be reliably

extracted from the bulk sediment and provide robust constraints on authigenic trace-metal distributions, pilot datasets for the full OAE 2 sedimentary sequence have been derived. Based on the observations presented in sections 4.2 and 4.3 for the test leachates, extraction using RT 6 M HCl was applied to a larger suite of samples from Mangaotane B (n = 43) and Sawpit Gully (n = 15).

Trace-element concentrations were obtained for the full suite of samples from Mangaotane B and Sawpit Gully and the U-isotope signature was obtained for the suite of grey shale samples from Mangaotane B. Uranium isotopes in leachates of red shales from Mangaotane B and grey shales from Sawpit Gully do not reliably represent the Fe- and Mn-(oxyhydr)oxide phase (section 4.3) and were therefore omitted from the remainder of the discussion. Correction for the detrital contribution was carried out in the same way as for the test leachates using Al-normalisation for all elements except U, which used Th-normalisation. Non-detrital Fe, Mn, Ni, Cr, V and U concentrations of both investigated New Zealand sections (Table S3 and Table S4) are shown relative to their C-isotope stratigraphies in Fig. 9a and c and the Mangaotane B U-isotope stratigraphy (Table S4) is displayed in Fig. 10.

The Fe_{corr} and Mn_{corr} distributions show small-scale variations across the lower Mangaotane B section in grey shale. Assuming that Fe_{corr} and Mn_{corr} have indeed formed authigenically, these patterns indicate a relatively stable Fe- and Mn-(oxyhydr)oxide content in the sediments and consequently locally stable oxic conditions during the pre-OAE 2 interval and through the early stages of the event, even though massive carbon drawdown and environmental degradation had commenced elsewhere, as well as during the first half of the period of climate cooling and partial environmental recovery known as the Plenus Cold Event or PCE (Fig. 9a). The same small-scale variability is observed for the other non-detrital metal concentrations of Ni, Cr and V. Across the second half of the trough in the C-isotope curve

related to the PCE, non-detrital Fe, Mn, Ni, Cr, and V concentrations at Mangaotane B show a progressive decrease (Fig. 9a). This trend can possibly be explained by the reductive dissolution of Fe- and Mn-(oxyhydr)oxides and the associated release of Ni, Cr, and V into the dissolved phase, lowering sedimentary concentrations, probably due to more reducing conditions at Mangaotane B. The agreement in the trends shown by most elements is interesting, as Cr_{corr} and V_{corr} may be associated with an authigenic phase other than Fe- and Mn-(oxyhydr)oxides, such as authigenic clays (section 4.2). By contrast, U_{corr} concentrations show an increase across the same stratigraphic interval. Due to its long oceanic residence time, the anomalously high amounts of U released from remote anoxic sinks due to oxidative liberation during the PCE, would have led to enriched U concentrations in the global ocean. This effect appears to be reflected in the increasing U_{corr} sedimentary record of Mangaotane B, and with elevated concentrations of U recorded at Eastbourne at the same time (Clarkson et al., 2018). Upon normalisation to Fe_{corr} and Mn_{corr} , increased concentrations across the second half of the trough in the C-isotope curve can also be observed in some of the other redox-sensitive elements (Fig. 9b). Interestingly, this effect seems to amplify with lengthening ocean residence time ($U > V > Cr > Ni$). This pattern shows that the oxidative liberation of redox-sensitive elements during the PCE, recorded in a number of sections (Jenkyns, et al., 2017) indeed had a global impact, however, only for elements with relatively long oceanic residence times.

At the base of the major red bed, Mn_{corr} concentrations show a sudden decrease (Fig. 9a). Non-detrital Fe concentrations express a similar pattern, after an initial excursion to higher concentrations. These elemental patterns point towards a reductive release of Fe- and Mn-(oxyhydr)oxides after the PCE. Non-detrital Ni and Cr concentrations follow this trend, once more confirming their association with Fe- and Mn-(oxyhydr)oxides. Non-detrital V concentrations show a sudden increase at the base of the red bed, which possibly suggests local V drawdown from the water column into the sediments during oxygen-deprived conditions, but

it is unclear from which sedimentary phase V would have been leached. These elemental patterns point towards less oxygenated conditions during red shale deposition, which contradicts the lithological evidence of red bed deposition and the decrease in TOC.

The $\delta^{238}\text{U}_{\text{corr}}$ for the pre-OAE 2 interval below the CIE in the grey shales of the Mangaotane B section (Fig 10) have an average value of -0.35 ± 0.18 ‰. Assuming that U released from Fe- and Mn-(oxyhydr)oxides is isotopically lighter than seawater by 0.19 to 0.29 ‰, this value corresponds to a seawater $\delta^{238}\text{U}$ ($\delta^{238}\text{U}_{\text{SW}}$) signature of -0.15 ± 0.18 ‰. (Goto et al., 2014). Both, the $\delta^{238}\text{U}_{\text{corr}}$ and the estimated $\delta^{238}\text{U}_{\text{SW}}$ overlap with the pre-OAE 2 seawater $\delta^{238}\text{U}$ of -0.40 ± 0.09 ‰ derived from the coeval pelagic chalks of the Eastbourne section (Clarkson et al., 2018). The congruence between these three values indicates that the Fe- and Mn-(oxyhydr)oxide phase in the Mangaotane B sediments may reflect the seawater $\delta^{238}\text{U}$ signature without significant U-isotope fractionation between seawater and Fe- and Mn-(oxyhydr)oxides. This possibility is supported by the findings of field adsorption experiments of U onto a variety of naturally occurring oxides, which showed negligible U-isotope fractionation (Shiel et al., 2013).

However, both, the $\delta^{238}\text{U}_{\text{corr}}$ and the estimated $\delta^{238}\text{U}_{\text{SW}}$ also overlap with the detrital $\delta^{238}\text{U}$ of -0.29 ± 0.03 ‰ (Andersen et al., 2017). In addition to this overlap, the characteristic negative $\delta^{238}\text{U}$ excursions present in the Eastbourne section could not be resolved at Mangaotane B. Also, while the very positive U-isotope value within the trough in the C-isotope curve could potentially indicate globally less U drawdown, similarly to the positive shift seen in the Eastbourne section, the shift only consists of a single sample and it is inconclusive whether the $\delta^{238}\text{U}$ values record seawater signatures. These observations suggest that neither the $\delta^{238}\text{U}_{\text{corr}}$ nor the estimated $\delta^{238}\text{U}_{\text{SW}}$ reflect the seawater signal. While seawater U-isotope signatures during OAE 2 could not be reliably extracted from any of the formations studied, the

relatively invariant $\delta^{238}\text{U}_{\text{corr}}$ across the grey shales of the Mangaotane B section (Fig. 10) in combination with the homogenous $\delta^{238}\text{U}$ signatures of the leaching experiments at Sawpit Gully (Fig. 5) strongly indicate that the leaching procedure itself does not generate U-isotope fractionation as an analytical artefact.

Non-detrital elemental concentrations in the Sawpit Gully section show no systematic trends, with the exception of one sample in the lower part of the C-isotope trough (Fig. 9c), which shows a decrease in Fe_{corr} , Ni_{corr} , Cr_{corr} , V_{corr} with a concomitant increase in Mn_{corr} . However, these results based on a single sample are not conclusive.

In conclusion, minor redox-sensitive elements in partial leachates of only the grey shales at Mangaotane B express variations that could possibly reflect changes in seawater compositions. Therefore, the Fe- and Mn-(oxyhydr)oxide phase in these samples likely contains elements directly incorporated or adsorbed from ambient seawater. Uranium-isotope ratios in these samples, however, do not exhibit systematic trends and are therefore unlikely to represent changes in ocean redox conditions. While the elemental patterns point towards less oxygenated conditions during red shale deposition, this interpretation contradicts the lithological evidence and could instead be the result of the change in the weathering regime of the sedimentary source areas. The lack of systematic trends in the Sawpit Gully stratigraphy does not allow for an unequivocal conclusion on the capability of selectively digesting and extracting the authigenic Fe- and Mn-(oxyhydr)oxide phase from these sediments.

4.5 *Implications for palaeo-redox reconstructions in red and grey shales*

The relatively large proportions of Mn and Fe leached during the partial digestions, compared with the relatively small proportions of detrital Al and other detrital elements

attacked simultaneously, points to the selective dissolution of the Fe- and Mn-(oxyhydr)oxide phase when red and grey shales are partially leached with RT 6 M HCl. While the successful extraction of the Fe- and Mn-(oxyhydr)oxide phase cannot unequivocally be identified as authigenic in origin, the coherent trace-metal stratigraphy in the Mangaotane B grey shales does suggest the potential of this unexplored phase as a palaeo-redox archive. Whilst leaching with RT 6 M HCl was the best of the tested methods, future studies with HCl of molarities between 1 and 6 are needed in order to further minimise the detrital contribution.

The inference that grey shales from Mangaotane B give the most reliable results is corroborated by Mn_{corr} concentrations that are about a factor of two higher than those recorded by red shales from Mangaotane B as well as grey shales from Sawpit Gully. Having said that, Fe_{corr} concentrations are comparable in grey shales from both sections, implying that the authigenic redox-sensitive elements mainly reside in Mn-(oxyhydr)oxides rather than Fe-(oxyhydr)oxides in the investigated sediments. The elemental concentration and $\delta^{238}U_{corr}$ variations across the Mangaotane B grey shales are nevertheless subtle, which is likely a result of the dominance of the detrital phase but also the relatively small U-isotope shifts expected during OAE 2.

We recommend sediments containing a Fe- and Mn-(oxyhydr)oxide fraction of at least 5 % and predominantly of authigenic origin, that could be identified, for example, using REE fractionation patterns, for the reconstruction of the palaeo-redox environment at the time of sedimentary deposition using red and grey shales. Provided these prerequisites are met, the Fe- and Mn-(oxyhydr)oxide fraction extracted from red or grey shales shows promise to serve as a robust archive for other redox-sensitive elements that primarily reside in this sedimentary phase, including Mn, Co and Ni, which display sizeable concentration variations that are not significantly impacted by detrital material, as is the case for U. Two observations are made for

the U- and Mo-isotope global palaeo-redox tracers in the context of red and grey shales. First, the reliable extraction of the authigenic U-isotope signature from the minor Fe- and Mn-(oxyhydr)oxide phase has been shown to be challenging due to the typically small variations of this heavy-element isotope system up-section in combination with comparatively low U concentrations in red and grey shales that are significantly influenced by detrital minerals. An investigation of red and grey shales deposited during another time period that documents larger, systematic variations in $\delta^{238}\text{U}$, would be required to further explore whether reliable information on marine redox state can be extracted from these sedimentary archives. For instance, time periods with more severe changes in ocean redox conditions like the Permian-Triassic Boundary event (252 Ma; Burgess et al., 2014) or the GOE would be good choices, preferably from pelagic settings with less detrital input. Second, the ability to extract reliable authigenic Mo-isotope signatures from red and grey shales is problematic due to the low levels of Mo in these sediments. Importantly, the extraction of reliable isotopic information for the other metals present in higher concentrations in the minor Fe- and Mn-(oxyhydr)oxide phase, such as Co and Ni, shows promise. To this end, the Co- and Ni-isotope systematics of red and grey shales may be capable of providing more robust constraints on palaeo-environmental conditions and should be further explored.

5 Conclusions

The majority of geochemical reconstructions of past ocean–atmosphere conditions are based on chemostratigraphic records for organic-rich black shales. However, these sedimentary archives form almost exclusively in lower latitudes, and are typically not deposited at mid- to high latitudes, leading to incomplete geographic coverage of the investigated palaeoceanographic phenomena. Within this study, the potential of oceanic ‘red beds’ and grey

shales were explored as new archives of past environmental conditions to complement the datasets derived from other lithologies. A series of leaching experiments were conducted, using progressively increasing reagent concentrations, with the purpose of extracting the authigenic, seawater-derived Fe- and Mn-(oxyhydr)oxide phase from Upper Cretaceous open-marine red and grey shales deposited as two sedimentary sections during OAE 2 (c. 94 Ma) along the continental margin of New Zealand, at high latitudes in the palaeo-Pacific Ocean. The chemostratigraphic records for a suite of redox-sensitive metals, as well as the $^{238}\text{U}/^{235}\text{U}$ ($\delta^{238}\text{U}$) global palaeo-redox tracer, were derived in order to develop an optimal method to selectively extract the authigenic Fe- and Mn-(oxyhydr)oxide fraction.

The relatively large proportions of Fe and Mn leached during the partial digestions with HCl and aqua regia, compared with relatively small proportions of detrital Al, indicate that the majority of the released Mn and Fe is of non-detrital origin. Furthermore, the enrichment of most elements that are strongly adsorbed onto Fe- and/or Mn-(oxyhydr)oxides in the partial digests and their correlation with Fe and Mn release suggests that the partial digestion approach of this study preferentially releases the Fe- and Mn-(oxyhydr)oxide phase from the bulk sample. However, the successful extraction of the Fe- and Mn-(oxyhydr)oxide phase cannot unequivocally be identified as being authigenic in origin. In contrast to these elements, U was probably extracted from a different authigenic fraction with very low U concentrations. Efforts to derive the authigenic U content proved promising for the grey shales at the Mangaotane B section, after applying a correction for detrital U contribution based on a baseline approach. A leaching procedure using RT 6 M HCl maximised extraction of the non-detrital component of trace metals while minimising the inherited detrital contribution. However, tests with HCl of molarities between 1 and 6 are advisable in order to further minimise the detrital contribution.

Extraction of the Fe- and Mn-(oxyhydr)oxide phase using RT 6 M HCl was applied across the entire stratigraphies of the two New Zealand sections and the coherent trace-metal stratigraphy in the Mangaotane B grey shales suggests the potential of this archive to be utilised for palaeo-redox studies. The results of this study indicate that the selective extraction of authigenic Fe- and Mn-(oxyhydr)oxide minerals from grey and potentially red shales offers promise for recording changes in the chemical state of the palaeo-oceans, provided the phase is predominantly of authigenic origin and its proportion within the bulk sediment is of sufficient magnitude (>5 %) to overcome the detrital contribution that confounds the interpretation of the geochemical data. These requirements seem to be met in the grey shales below the major red bed in the Mangaotane B section spanning the first half of OAE 2, where the chemostratigraphy appears to reflect changes in marine redox conditions. Specifically, an increase in redox-sensitive element concentrations demonstrates the global impact of the PCE, albeit only for elements with relatively long oceanic residence times. This conclusion, however, does not apply to the U-isotope and Mo-isotope global palaeo-redox tracers, as the $\delta^{238}\text{U}$ signature lacked consistency and the Mo-isotope signature could not be acquired due to post-depositional Mo loss from the sediments. Moreover, the results of this study indicate that red and grey shales are a well-suited archive for reconstructing palaeo-redox variations utilising Fe, Mn, Co and Ni and, where applicable, their isotopic systems. Study of these elements could form the focus of ongoing palaeo-environmental reconstructions using red and grey shales. In contrast to the grey shales at Mangaotane B, the Fe- and Mn-(oxyhydr)oxide phase appears to be insufficient in the other formations studied to reliably reflect the seawater chemistry of the south-west Pacific Ocean during OAE 2.

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FIGURE AND TABLE CAPTIONS:

Fig. 1: Global oceanic coverage of (a) black shales during OAE 2 (93 Ma) and (b) red beds 80 Ma, after OAE 2 (Wang et al., 2011). (c) Panthalassic reconstruction indicating locations of sections: Mangaotane B and Sawpit Gully (modified from Zhou et al., 2015). Yellow indicates continental crust, light blue indicates continental shelf areas and turquoise indicates oceanic crust. (d) Map of central New Zealand showing the sampling sites Sawpit Gully and Mangaotane B (modified from Hasegawa et al., 2013). Grey areas indicate occurrences of Albian–Maastrichtian rocks (113 Ma–66 Ma).

Fig. 2: (a) Stratigraphy, magnetic susceptibility (MS), weight-per-cent total organic carbon (wt % TOC) and $\delta^{13}\text{C}_{\text{TOC}}$ data from (a) Mangaotane B (black data points derive from samples with TOC > 0.1 wt % representing global signatures; grey data points derive from samples with TOC $\leq$ 0.1 wt %) and from (b) Sawpit Gully (Gangl et al., 2019). Coloured bands describe the carbon-isotope stages. Stratigraphic positions of samples chosen for partial extraction experiments are indicated by arrows.

Fig. 3: Distribution patterns of elements in the different acid-leached fractions in samples from (a) Mangaotane B and (b) Sawpit Gully. Uncertainties are given as 2 SD.

Fig. 4: Distribution patterns of redox-sensitive elements normalised to Al in whole-rock digests of samples from Mangaotane B and Sawpit Gully in comparison to the upper continental crust (UCC; Rudnick and Gao, 2014) and the Torlesse Composite Terrane (Price et al., 2015). The chemical index of alteration (CIA) is defined as molar ratio of $\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})$ where CaO^* is corrected to remove the contribution of carbonate and apatite (McLennan, 1993; Nesbitt and Young, 1982). Uncertainties are given as 2 SD.

1089 **Fig. 5:** $\delta^{238}\text{U}$ signatures in extractions and total digests of the samples from (a–c)
1090 Mangaotane B and (d–f) Sawpit Gully. Uncertainties are given as 2 SE.

1091 **Fig. 6:** Cross-plots of minor redox-sensitive elements against Al concentrations in sample
1092 leachates compared to compositions in their whole-rock digests and the Torlesse Composite
1093 Terrane (Price et al., 2015).

1094 **Fig. 7:** Cross-plots of minor redox-sensitive elements against Fe and Mn concentrations in
1095 sample leachates compared to compositions in their whole-rock digests.

1096 **Fig. 8:** Measured metal concentrations and concentrations corrected for detrital inputs in
1097 sample leachates of Mangaotane B and Sawpit Gully.

1098 **Fig. 9:** Concentrations of redox-sensitive elements corrected for detrital contributions relative
1099 to the $\delta^{13}\text{C}_{\text{TOC}}$ stratigraphies from (a) Mangaotane B and (c) Sawpit Gully in comparison to
1100 Eastbourne, UK. Panel (b) shows redox-sensitive elements from Mangaotane B corrected for
1101 detrital contributions and normalised to Fe_{corr} and Mn_{corr} across the trough of the C-isotope
1102 curve. Coloured bands describe the carbon-isotope stages. Uncertainties are given as 2 SD.

1103 **Fig. 10:** U-isotope values corrected for detrital contributions relative to the $\delta^{13}\text{C}_{\text{TOC}}$
1104 stratigraphies from Mangaotane B in comparison to Eastbourne, UK. Coloured bands describe
1105 the carbon-isotope stages. Uncertainties are given as 2 SE.

1106 **Table 1:** Elemental concentrations (in $\mu\text{g/g} \pm 2 \text{ SD}$) in leachates from Mangaotane B and
1107 Sawpit Gully, New Zealand

1108 **Table 2:** U-isotope ratios measured and corrected for detrital contribution (± 2 SE) and U
1109 concentrations corrected for detrital contribution (± 2 SD) in leachates from Mangaotane B and
1110 Sawpit Gully, New Zealand

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Table 1: Elemental concentrations (in µg/g ± 2 SD) in leachates from Mangaotane B and Sawpit Gully, New Zealand

			Redox-sensitive metals															
Mangaotane B			Fe	± 2 SD	Mn	± 2 SD	Co	± 2 SD	Ni	± 2 SD	Mo	± 2 SD	Cr	± 2 SD	V	± 2 SD	U	± 2 SD
RT 1 M HCl	pre-OAE 2	21.42	11970	754	247	16	4.74	0.28	11.02	0.62	<LoD	n/a	5.61	0.50	8.48	0.46	0.092	0.010
	early-OAE 2	24.33	13829	871	331	21	3.81	0.22	8.11	0.45	<LoD	n/a	5.95	0.53	7.52	0.41	0.0777	0.0085
	late-OAE 2	32.01	4483	282	123.0	7.7	2.27	0.13	3.20	0.18	<LoD	n/a	1.89	0.17	2.36	0.13	0.115	0.013
RT 6 M HCl	pre-OAE 2	21.42	23858	1503	464	29	9.10	0.54	21.2	1.2	<LoD	n/a	13.2	1.2	18.1	1.0	0.108	0.012
	early-OAE 2	24.33	26018	1639	581	37	7.76	0.46	16.22	0.91	<LoD	n/a	13.0	1.2	16.59	0.90	0.088	0.010
	late-OAE 2	32.01	15891	1001	288	18	6.82	0.40	11.69	0.65	0.0640	0.0084	8.38	0.75	16.05	0.87	0.245	0.027
hot 6 M HCl	pre-OAE 2	21.42	23837	1502	459	29	9.01	0.53	21.4	1.2	<LoD	n/a	12.9	1.2	18.0	1.0	0.117	0.013
	early-OAE 2	24.33	25502	1607	566	36	7.78	0.46	16.41	0.92	<LoD	n/a	12.5	1.1	15.46	0.83	0.088	0.010
	late-OAE 2	32.01	14530	915	259	16	5.84	0.34	9.66	0.54	0.0685	0.0090	7.06	0.63	15.24	0.82	0.238	0.026
hot 10 M HCl	pre-OAE 2	21.42	23833	1501	463	29	9.00	0.53	21.2	1.2	<LoD	n/a	13.5	1.2	18.3	1.0	0.124	0.014
	early-OAE 2	24.33	25673	1617	576	36	7.77	0.46	16.55	0.93	<LoD	n/a	13.5	1.2	15.87	0.86	0.095	0.010
	late-OAE 2	32.01	17162	1081	306	19	7.39	0.44	12.70	0.71	0.0725	0.0095	8.67	0.77	17.57	0.95	0.288	0.032
aqua regia	pre-OAE 2	21.42	27167	1712	514	32	11.05	0.65	24.4	1.4	0.0308	0.0040	15.9	1.4	24.2	1.3	0.259	0.028
	early-OAE 2	24.33	27067	1705	599	38	8.55	0.50	18.0	1.0	<LoD	n/a	14.4	1.3	19.9	1.1	0.199	0.022
	late-OAE 2	32.01	19107	1204	332	21	8.45	0.50	15.59	0.87	0.079	0.010	11.3	1.0	20.9	1.1	0.401	0.044
whole-rock digest	pre-OAE 2	21.42	33045	2082	542	34	11.48	0.68	25.5	1.4	0.133	0.017	44.1	3.9	102.3	5.5	3.02	0.33
	early-OAE 2	24.33	35260	2221	664	42	9.76	0.58	20.0	1.1	0.139	0.018	44.9	4.0	92.0	5.0	2.52	0.28
	late-OAE 2	32.01	29991	1889	426	27	10.71	0.63	19.0	1.1	0.199	0.026	41.2	3.7	82.3	4.4	2.59	0.28
Sawpit Gully			Fe	± 2 SD	Mn	± 2 SD	Co	± 2 SD	Ni	± 2 SD	Mo	± 2 SD	Cr	± 2 SD	V	± 2 SD	U	± 2 SD
RT 1 M HCl	pre-OAE 2	3.82	15288	841	143.1	1.6	9.05	0.12	14.63	0.29	0.125	0.013	9.95	0.18	16.08	0.47	0.1097	0.0093
	early-OAE 2	5.53	12142	668	117.4	1.3	6.978	0.091	9.27	0.19	0.189	0.019	8.91	0.16	12.98	0.38	0.136	0.012
	late-OAE 2	32.95	14887	819	129.5	1.4	6.125	0.080	9.39	0.19	0.0846	0.0085	9.03	0.16	15.68	0.45	0.120	0.010
RT 6 M HCl	pre-OAE 2	3.82	22818	1255	224.9	2.5	11.01	0.14	19.05	0.38	0.292	0.029	15.57	0.28	23.84	0.69	0.156	0.013
	early-OAE 2	5.53	18980	1044	202.1	2.2	9.15	0.12	14.52	0.29	0.440	0.044	14.83	0.27	20.40	0.59	0.193	0.016
	late-OAE 2	32.95	23740	1306	226.8	2.5	8.58	0.11	14.93	0.30	0.138	0.014	16.65	0.30	25.54	0.74	0.156	0.013
hot 6 M HCl	pre-OAE 2	3.82	22665	1247	224.3	2.5	11.28	0.15	19.45	0.39	0.300	0.030	16.19	0.29	24.44	0.71	0.163	0.014
	early-OAE 2	5.53	19168	1054	200.7	2.2	9.34	0.12	14.60	0.29	0.393	0.040	15.28	0.27	20.87	0.61	0.200	0.017
	late-OAE 2	32.95	23813	1310	219.6	2.4	8.38	0.11	14.84	0.30	0.108	0.011	16.60	0.30	24.90	0.72	0.184	0.016
hot 10 M HCl	pre-OAE 2	3.82	22658	1246	224.9	2.5	11.30	0.15	19.82	0.40	0.310	0.031	16.28	0.29	24.38	0.71	0.169	0.014
	early-OAE 2	5.53	18920	1041	198.6	2.2	9.36	0.12	14.33	0.29	0.462	0.047	15.03	0.27	20.47	0.59	0.218	0.019
	late-OAE 2	32.95	23905	1315	220.8	2.4	8.51	0.11	14.94	0.30	0.104	0.010	16.72	0.30	24.75	0.72	0.190	0.016
aqua regia	pre-OAE 2	3.82	36032	1982	244.7	2.7	13.55	0.18	27.73	0.55	0.591	0.060	19.21	0.35	28.98	0.84	0.356	0.030
	early-OAE 2	5.53	25852	1422	246.5	2.7	10.97	0.14	18.57	0.37	0.759	0.077	17.26	0.31	24.55	0.71	0.404	0.034
	late-OAE 2	32.95	26997	1485	236.8	2.6	9.22	0.12	16.87	0.34	0.149	0.015	18.95	0.34	29.65	0.86	0.375	0.032
whole-rock digest	pre-OAE 2	3.82	38958	2143	304.5	3.3	14.38	0.19	30.23	0.60	0.801	0.081	53.36	0.96	84.2	2.4	2.65	0.23
	early-OAE 2	5.53	30825	1695	308.1	3.4	11.96	0.16	20.70	0.41	0.99	0.10	51.71	0.93	76.3	2.2	2.90	0.25
	late-OAE 2	32.95	33733	1855	302.6	3.3	10.81	0.14	20.62	0.41	0.321	0.032	51.11	0.92	90.6	2.6	2.99	0.25

Table 1: Elemental concentrations (in $\mu\text{g/g} \pm 2 \text{ SD}$) in leachates from Mangaotane B and Sawpit Gully, New Zealand (continued)

			Detrital metals							
Mangaotane B										
Extraction	Sample	Depth (m)	Al	± 2 SD	Th	± 2 SD	Ti	± 2 SD	Zr	± 2 SD
RT 1 M HCl	pre-OAE 2	21.42	5893	454	0.759	0.029	10.50	0.62	0.0402	0.0015
	early-OAE 2	24.33	6480	499	0.717	0.027	9.15	0.54	0.0421	0.0016
	late-OAE 2	32.01	2490	192	1.050	0.040	5.55	0.33	0.0399	0.0015
RT 6 M HCl	pre-OAE 2	21.42	11569	891	1.184	0.045	113.9	6.7	1.358	0.052
	early-OAE 2	24.33	12294	947	1.100	0.042	97.9	5.8	1.294	0.049
	late-OAE 2	32.01	6523	502	2.481	0.094	205	12	2.96	0.11
hot 6 M HCl	pre-OAE 2	21.42	11639	896	1.207	0.046	125.0	7.4	1.021	0.039
	early-OAE 2	24.33	11867	914	0.980	0.037	86.8	5.1	1.037	0.039
	late-OAE 2	32.01	5544	427	2.416	0.092	188	11	2.66	0.10
hot 10 M HCl	pre-OAE 2	21.42	11706	901	1.322	0.050	170	10	1.771	0.067
	early-OAE 2	24.33	12156	936	1.147	0.044	109.3	6.5	1.477	0.056
	late-OAE 2	32.01	6935	534	2.63	0.10	202	12	3.15	0.12
aqua regia	pre-OAE 2	21.42	14473	1114	3.48	0.13	906	53	4.80	0.18
	early-OAE 2	24.33	14080	1084	2.97	0.11	722	43	4.35	0.17
	late-OAE 2	32.01	9885	761	4.05	0.15	605	36	5.38	0.20
whole-rock digest	pre-OAE 2	21.42	85488	6583	13.06	0.50	4366	258	130.7	5.0
	early-OAE 2	24.33	85775	6605	13.21	0.50	4631	273	139.7	5.3
	late-OAE 2	32.01	82546	6356	12.04	0.46	4179	247	132.0	5.0
Sawpit Gully										
RT 1 M HCl	pre-OAE 2	3.82	6499	78	1.1292	0.0068	14.71	0.26	0.0273	0.0010
	early-OAE 2	5.53	5768	69	1.1393	0.0068	17.05	0.31	0.0384	0.0015
	late-OAE 2	32.95	6568	79	1.1673	0.0070	19.16	0.34	<LoD	n/a
RT 6 M HCl	pre-OAE 2	3.82	10544	127	2.523	0.015	118.5	2.1	2.574	0.098
	early-OAE 2	5.53	9587	115	2.441	0.015	128.2	2.3	2.66	0.10
	late-OAE 2	32.95	11315	136	2.703	0.016	145.2	2.6	2.54	0.10
hot 6 M HCl	pre-OAE 2	3.82	10847	130	2.510	0.015	97.0	1.7	1.950	0.074
	early-OAE 2	5.53	9888	119	2.557	0.015	96.4	1.7	1.831	0.070
	late-OAE 2	32.95	11439	137	2.844	0.017	99.0	1.8	1.860	0.071
hot 10 M HCl	pre-OAE 2	3.82	10950	131	2.685	0.016	139.1	2.5	2.96	0.11
	early-OAE 2	5.53	9824	118	2.924	0.018	152.2	2.7	2.99	0.11
	late-OAE 2	32.95	11383	137	2.964	0.018	157.1	2.8	3.67	0.14
aqua regia	pre-OAE 2	3.82	12941	155	4.180	0.025	468.7	8.4	5.93	0.23
	early-OAE 2	5.53	11371	136	4.264	0.026	352.3	6.3	5.43	0.21
	late-OAE 2	32.95	13310	160	4.256	0.026	357.4	6.4	4.98	0.19
whole-rock digest	pre-OAE 2	3.82	74098	889	11.589	0.070	4291	77	131.1	5.0
	early-OAE 2	5.53	73726	885	13.361	0.080	4328	78	143.8	5.5
	late-OAE 2	32.95	77450	929	13.018	0.078	4685	84	136.5	5.2

Table 2: U-isotope ratios measured and corrected for detrital contribution (± 2 SE) and U concentrations corrected for detrital contribution (± 2 SD) in leachates from Mangaotane B and Sawpit Gully, New Zealand

		Mangaotane B							Sawpit Gully						
Extraction	Sample	Depth (m)	$\delta^{238}\text{U}$ (‰)	2 SE	$\delta^{238}\text{U}_{\text{corr}}$ (‰)	2 SE	U_{corr} (µg/g)	2 SD	Depth (m)	$\delta^{238}\text{U}$ (‰)	2 SE	$\delta^{238}\text{U}_{\text{corr}}$ (‰)	2 SE	U_{corr} (µg/g)	2 SD
RT 1 M HCl	pre-OAE 2	21.42	-0.272	0.081	-0.246	0.074	0.048	0.011	3.82	-0.243	0.081	-0.210	0.058	0.074	0.014
	early-OAE 2	24.33	-0.222	0.072	-0.130	0.075	0.036	0.010	5.53	-0.296	0.092	-0.300	0.060	0.099	0.016
	late-OAE 2	32.01	-0.223	0.097	-0.13	0.10	0.054	0.014	32.95	-0.160	0.087	-0.095	0.061	0.083	0.015
RT 6 M HCl	pre-OAE 2	21.42	-0.364	0.061	-0.481	0.081	0.039	0.015	3.82	-0.296	0.087	-0.300	0.086	0.076	0.030
	early-OAE 2	24.33	-0.310	0.056	-0.34	0.10	0.024	0.013	5.53	-0.279	0.081	-0.266	0.065	0.115	0.030
	late-OAE 2	32.01	-0.358	0.055	-0.443	0.064	0.102	0.032	32.95	-0.189	0.082	-0.041	0.091	0.070	0.031
hot 6 M HCl	pre-OAE 2	21.42	-0.205	0.081	-0.059	0.098	0.047	0.016	3.82	-0.300	0.080	-0.3000	0.0045	0.082	0.030
	early-OAE 2	24.33	-0.283	0.081	-0.25	0.11	0.031	0.012	5.53	-0.292	0.087	-0.283	0.071	0.119	0.030
	late-OAE 2	32.01	-0.357	0.080	-0.441	0.094	0.098	0.031	32.95	-0.223	0.082	-0.136	0.078	0.093	0.033
hot 10 M HCl	pre-OAE 2	21.42	-0.280	0.092	-0.25	0.11	0.048	0.017	3.82	-0.257	0.081	-0.215	0.079	0.083	0.032
	early-OAE 2	24.33	-0.290	0.080	-0.26	0.13	0.028	0.014	5.53	-0.310	0.088	-0.318	0.074	0.125	0.034
	late-OAE 2	32.01	-0.432	0.080	-0.586	0.082	0.135	0.035	32.95	-0.265	0.087	-0.238	0.083	0.095	0.035
aqua regia	pre-OAE 2	21.42	-0.389	0.079	-0.77	0.18	0.057	0.040	3.82	-0.239	0.073	-0.202	0.056	0.222	0.052
	early-OAE 2	24.33	-0.401	0.079	-1.6	6.8	0.025	0.034	5.53	-0.283	0.074	-0.269	0.053	0.267	0.055
	late-OAE 2	32.01	-0.415	0.067	-0.583	0.078	0.166	0.052	32.95	-0.214	0.081	-0.157	0.062	0.239	0.052
whole rock digest	pre-OAE 2	21.42	-0.331	0.082	n.a.	n.a.	n.a.	n.a.	3.82	-0.329	0.086	n.a.	n.a.	n.a.	n.a.
	early-OAE 2	24.33	-0.358	0.083	n.a.	n.a.	n.a.	n.a.	5.53	-0.274	0.073	n.a.	n.a.	n.a.	n.a.
	late-OAE 2	32.01	-0.329	0.083	n.a.	n.a.	n.a.	n.a.	32.95	-0.313	0.079	n.a.	n.a.	n.a.	n.a.