Cambridge University Press
978-1-108-79794-8 — Vanadium Isotopes
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1 Introduction

There is great interest in understanding how the concentration of oxygen evolved in the ocean and atmosphere over geological time because it has direct links to, for example, the evolution of photosynthesis, emergence of macroscopic life forms, and mass extinction events. Most commonly, evolution of the marine oxygen reservoir is studied via chemical or biomarker proxies that are sensitive to changes in the redox state of the sediment depositional environment (Canfield et al., 2018; Tribovillard et al., 2006). It has long been recognized that the concentrations of different trace metals in sediments depend strongly on the redox state of the overlying water column as well as the overall supply rate of the metal to seawater (Tribovillard et al., 2006). In turn, marine input fluxes can depend strongly on atmospheric oxygen concentrations, which can be independent of water-column oxygen concentrations (Anbar et al., 2007). However, trace metal concentrations in low-oxygen sediments are also controlled by the mechanisms of enrichment, which are affected by local processes such as basinal restriction and redistribution of Fe and Mn oxides from shallower, oxic portions of the seafloor (Algeo, 2004; McArthur et al., 2008; Ostrander et al., 2019b; Owens et al., 2012). Hence, trace metal concentrations alone can in principle be interpreted in terms of changes in either the oceanic or the atmospheric oxygen reservoirs or, alternatively, changes in the local depositional environment, depending on which process(es) each element is controlled by.

In the last two decades, stable isotopic studies of a host of these trace metals, like Fe, Mo, U, Tl, Se, and Cr (Frei et al., 2009; Kendall et al., 2017; Lau et al., 2019; Ostrander et al., 2019a; Stüeken et al., 2015), have been utilized to gain further insight into past oxygen fluctuations because stable isotope variations, in concert with concentrations, potentially can be used to disentangle effects from ocean–atmosphere redox and local depositional effects, which is more challenging with concentrations alone. Metal stable isotope fractionation is typically most pronounced for isotopic equilibria between species with different redox states (Bigeleisen and Mayer, 1947), which is the reason why most of these isotope systems have found utility as redox proxies. Such species equilibria, or redox couples, occur at different levels of redox potential (Rue et al., 1997), such that metal stable isotope variations in sediments are likely indicators of specific levels on a redox ladder (figure 1 in Owens, 2019). Essentially all the metals utilized to date as paleo-redox proxies have redox couples significantly below the O_2–H_2O redox couple. Therefore, these metal isotope proxies may provide information about past changes in ocean redox but can be difficult to utilize as proxies for how much oxygen was present at the time of deposition.

However, many geologically important events, such as ocean anoxic events (OAEs), the Permo-Triassic mass extinction, and the Cambrian explosion, all occurred at times when the oceans were likely fully or at least partially oxygenated relative to today (Jenkyns, 2010; Lu et al., 2018; Lyons et al., 2014). Thus, changes in ocean oxygenation during these periods likely transitioned across moderately oxygenated conditions, which may be difficult to detect with existing isotope proxies.

The element vanadium (V) potentially is different from other metals used as isotope redox proxies because it consists of multiple redox couples, the most oxic of which may operate at nonzero oxygen concentrations (Gustafsson, 2019; Wehrli and Stumm, 1989). Specifically, V can occur as V(III), V(IV), and V(V) in different marine sediment depositional environments (Gustafsson, 2019; Wehrli and Stumm, 1989). In open ocean, fully oxygenated seawater, V is exclusively present as vanadate (VO_4^{3-}) or its hydrolyzed versions (HVO_4^{2-}, $H_2VO_4^{-}$). However, at low oxygen, vanadate is reduced to vanadyl (VO^{2+}) or its hydrolyzed versions ($VO(OH)^{+}$, $VO(OH)_2$). In addition, the stability of vanadyl at higher redox potentials is augmented by the presence of organic ligands (Wehrli and Stumm, 1989). Therefore, it is likely that the VO_4^{3-}–VO^{2+} redox couple operates at nonzero oxygen concentrations, which opens the potential for using V isotopes as an indicator for the level of marine oxygenation rather than, for example, areal extent of anoxia or euxinia, as has been suggested for other metal isotope proxies.

High-precision measurements of V isotope ratios ($\delta^{51}V = 1000\times[(^{51}V/^{50}V_{sample} - {}^{51}V/^{50}V_{AA})/{}^{51}V/^{50}V_{AA}]$) have only recently been developed (Nielsen et al., 2011; Nielsen et al., 2016; Prytulak et al., 2011; Wu et al., 2016), primarily because V has only two isotopes (^{50}V and ^{51}V) and the low abundance of ^{50}V (~0.24 percent) makes it very difficult to obtain precise and accurate isotope ratios. Therefore, there is still much to learn about the conditions under which V isotopes might be used as a paleo-redox proxy, as well as which sediment archives are most appropriate for exploring V isotope variations. In the following, I first review the marine elemental and isotopic cycles for V, followed by an outline of the analytical methods required for precise and accurate V isotope measurements. Lastly, I discuss during which geological time periods and in which sedimentary archives V isotopes are most likely to find utility in the future.

2 Marine Elemental and Isotopic Cycle of Vanadium

The marine mass balance of V has been the subject of multiple previous studies (Emerson and Huested, 1991; Morford and Emerson, 1999). However, since the most recent assessment, several findings that affect the input and output fluxes of V have been published, which I here use to reassess the marine elemental V budget. Subsequently, I couple the elemental mass balance with recent V isotope data for marine sediments to construct a marine isotopic budget for V.

2.1 Elemental V Mass Balance

There are five principal marine V fluxes: rivers, hydrothermal sediments, oxic sediments, euxinic sediments, and anoxic sediments (Figure 1). The V concentration of open ocean oxygenated seawater is, based on the most recent GEOTRACES data (Ho et al., 2018), relatively invariant globally at ~35 nmol/kg, which is consistent with the first V determinations of seawater (Collier, 1984; Jeandel et al., 1987) and implies that all the major ocean basins have essentially invariant V concentrations. Surface seawater is only mildly depleted in V (~10 percent relative to deep water) and, because the minor V uptake into particulate material at the surface is remineralized at depth in oxygenated seawater (Collier, 1984), particulates from oxic portions of the water column are unlikely to have a profound effect on the overall marine V mass balance.

Rivers constitute a major input of V to the ocean. The riverine V input flux has been investigated relatively extensively and the most recent compilation of river concentration data concluded that the global V flux to the ocean is 520 Mmol/yr (Shiller and Mao, 2000). These data also include considerations of different weathering styles, source rock compositional variations, and estuarine processes (Shiller and Boyle, 1987; Shiller and Mao, 2000), making this a relatively robust number.

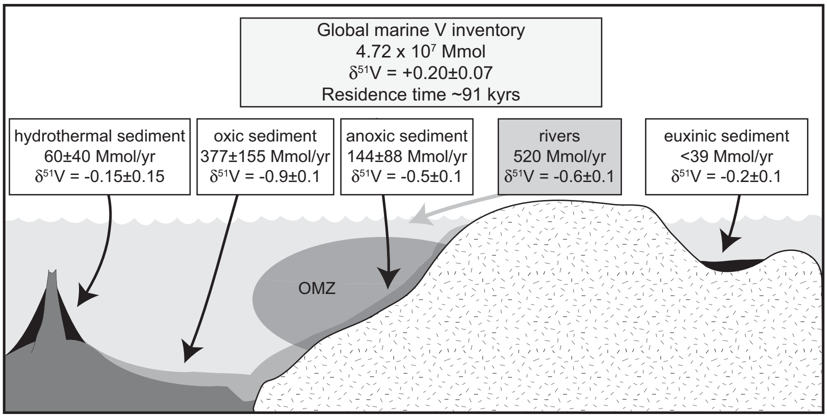

Figure 1 Summary of the fluxes and isotope compositions of the major marine inputs and outputs for V. Details of fluxes and their calculated magnitudes are described in the text. Isotope compositions taken from Schuth et al. (2019); Wu et al. (2017); Wu et al. (2019a); Wu et al. (2020).

Hydrothermal sediments represent a significant marine V sink due to sorption onto or coprecipitation with Fe oxides (Trefry and Metz, 1989). Previous estimates of this V flux reported values of 140 and 430 Mmol/yr (Rudnicki and Elderfield, 1993; Trefry and Metz, 1989). These estimates were based on the relatively invariant V/Fe ~ 4×10^{-3} in hydrothermal sediments (Trefry and Metz, 1989). When this ratio was combined with the average Fe concentration of endmember hydrothermal fluids (~1 mmol/kg), an average Fe precipitation efficiency of 50 and 100 percent, respectively, and a hydrothermal fluid flux ($HT_{FluidFlux}$) of 7 and 10×10^{13} kg/yr, respectively, then the two estimates were obtained. The best estimates for the average V/Fe ratio of hydrothermal sediments ($V/Fe_{HT\text{-}seds}$) and Fe concentrations in hydrothermal fluids ($Fe_{HT\text{-}fluid}$) remain the same as previously, and the best estimate for Fe precipitation efficiency ($Fe_{PrecEff}$) is likely still ~100 percent (Rudnicki and Elderfield, 1993), even considering that significant amounts of hydrothermal dissolved Fe can be traced over large distances in the ocean (Fitzsimmons et al., 2014; Fitzsimmons et al., 2017; Tagliabue et al., 2010). However, the most recent estimates for high-temperature hydrothermal fluid fluxes are substantially lower than earlier values. The most comprehensive recent estimates reveal values of ~$0.6\text{–}2.5 \times 10^{13}$ kg/yr (Coogan and Dosso, 2012; Nielsen et al., 2017; Teagle et al., 2003), about an order of magnitude lower than what was previously used to calculate V fluxes into hydrothermal sediments ($V_{HT\text{-}flux}$). As in previous studies, the parameters mentioned are combined in the equation:

$$V_{HT\text{-}flux} = (V/Fe)_{HT\text{-}seds} \times Fe_{HT\text{-}fluid} \times Fe_{PrecEff} \times HT_{FluidFlux} \qquad (1)$$

This yields a best estimate of 60 ± 40 Mmol/yr for the hydrothermal V output flux if we implement a hydrothermal fluid flux of $1.5 \pm 1 \times 10^{13}$ kg/yr, which renders hydrothermal V output fluxes significantly smaller than previously thought.

Oxic sediments are known to accumulate substantial amounts of V through adsorption onto Fe oxyhydroxides and Mn oxides and constitute an output flux. An earlier estimate separated oxic sediments into pelagic clays/carbonates and ferromanganese (Fe-Mn) crusts/nodules and listed fluxes of 430 and 80 Mmol/yr (Morford and Emerson, 1999), respectively, although the method for calculating these fluxes was not detailed. Here, published authigenic V fluxes to pelagic sediments of 0.12 ± 0.05 $\mu mol/cm^2 \times kyr$ (Thomson et al., 1984) are used in combination with the total area of pelagic sedimentation of 3.11×10^{18} cm^2 (Southam and Hay, 1977). This yields a V flux associated with pelagic clays of 373 ± 155 Mmol/yr, which is within error of the previous estimate for pelagic clays. However, further studies of the V flux into pelagic clays would be likely to constrain this number significantly better. Ferromanganese crusts and nodules have V concentrations of ~400–800 µg/g (Hein et al., 2003; Wu et al., 2019b), and the total mass of Fe-Mn crusts and nodules on the ocean floor has been estimated to be ~1 × 10^{18} g (Hein et al., 2003). Using a very conservatively low average age for the base layer of these deposits of 2 Ma (Rehkämper and Nielsen, 2004) results in an annual V flux associated with Fe-Mn crusts and nodules of ~6 ± 2 Mmol/yr. This value should be seen as an absolute maximum, given that most of these Fe-Mn deposits are likely older than the 2 Ma used here. Hence, V fluxes associated with Fe-Mn deposits (nonhydrothermal) can be considered negligible in the global marine V mass balance.

Sediments deposited in low oxygen environments, in particular those with high organic carbon contents, are generally enriched in V relative to crustal values (Calvert and Pedersen, 1993; Morford and Emerson, 1999). Typically, these enrichments have been ascribed to diffusional transport of V across the sediment–water interface in low-oxygen conditions (Calvert and Pedersen, 1993; Francois, 1988; Morford and Emerson, 1999). However, several recent studies have investigated the V abundances in marine particles from oxic (South Pacific), anoxic (Peru Margin oxygen minimum zone or OMZ), and euxinic (Cariaco Basin) settings (Calvert et al., 2015; Ho et al., 2018; Ohnemus et al., 2017). These data reveal that marine particulates collected from oxic seawater are generally not significantly enriched relative to average crustal abundances, in agreement with earlier work (Collier, 1984). This finding was independent of organic matter, Fe, and P contents (Ho et al., 2018; Ohnemus et al., 2017), implying that biological utilization of V by primary producers is relatively minor. On the other hand, all particle samples collected from anoxic or euxinic water masses uniformly reveal substantial V enrichments relative to crustal backgrounds. Furthermore, the level of enrichment in these particles is similar to those found in organic-rich anoxic and euxinic sediments (Calvert et al., 2015). Although there is significant uncertainty in the exact process responsible for the V enrichment, most likely, vanadate is reduced at low oxygen to vanadyl species, which are subsequently incorporated into organic matter through either a biotic or an abiotic pathway (Ohnemus et al., 2017). Vanadyl species are particularly susceptible to incorporation into tetrapyrroles, which are decay products of chlorophyll; this also accounts for the high V concentrations in many crude oils (Lewan and Maynard, 1982). It is notable that several earlier studies investigating V contents in marine particles collected with sediment traps in both anoxic and euxinic waters found no enrichment in particulate V relative to crustal values (Francois, 1988; Nameroff et al., 2002). The more recent studies include particles collected using both in-situ pumps (Ho et al., 2018; Ohnemus et al., 2017) and sediment traps (Calvert et al., 2015); hence, the origin of these apparent discrepancies is not clear. However, it has previously been argued that sediment trap material can lose significant amounts of authigenic constituents before sample recovery (Kumar et al., 1996), potentially accounting for the lower V in sediment trap particles.

As outlined earlier, the stability of V(IV) species is not only dependent on oxygen concentrations; they are also preferentially stabilized in the presence of organic ligands (Beck et al., 2008; Brumsack and Gieskes, 1983; Emerson and Huested, 1991; Wehrli and Stumm, 1989), which can make it difficult to predict the oxygen content at which V is most efficiently incorporated into marine particles. However, most studies have found that anoxic (here defined as predominantly without oxygen at and above the sediment–water interface, such as the Santa Barbara Basin and the most pronounced OMZs) and euxinic (here defined as predominantly sulfidic at and above the sediment–water interface, for example observed in the Black Sea, Saanich Inlet, and Cariaco Basin) sediments are more enriched in V than suboxic sediments (here defined as sediments where oxygen penetrates <3 cm into the sediment due to lowered bottom water (BW) oxygen contents or high rates of oxygen consumption within the sediment, observed, for example, in many OMZs and coastal regions that are not strongly stratified). This general pattern of V enrichment implies that reduction of vanadate is most efficient at close to zero oxygen. In addition, it has been shown that further reduction of vanadyl to insoluble trivalent V species in euxinic environments is not kinetically favorable (Wanty and Goldhaber, 1992), which may explain why particles and sediments in euxinic basins exhibit similar enrichments to those in anoxic environments. Vanadyl may also adsorb to oxides within the sediment (Wehrli and Stumm, 1989), although the Fe and Mn oxides typically responsible for V enrichment in oxic sediments are often reductively dissolved in low-oxygen sediments, thus eliminating this process as a likely vector of V enrichment except potentially under the operation of an Fe oxide shuttle (Scholz et al., 2011).

In terms of fluxes, previous studies have inferred that V is added to the ocean via release of V-rich porewaters from suboxic sediments (Morford and Emerson, 1999; Morford et al., 2005; Shaw et al., 1990). One study concluded that 300–800 Mmol/yr of V was added to the ocean via this mechanism (Morford and Emerson, 1999). This range of values was determined by comparing V/Al ratios in bulk suboxic sediments with those found in post-Archean Australian shales (PAAS; Nance and Taylor, 1976) and observing that PAAS had higher V/Al ratios than some suboxic sediments. However, many shales are enriched in V relative to crustal values because they were deposited in low-oxygen environments, and, therefore, it has been argued (Nameroff et al., 2002) that a more appropriate comparison to assess whether suboxic sediments are enriched or depleted in V is average upper continental crust (Rudnick and Gao, 2003) or crustal compositions from the most proximal source relative to the marine sediment studied (Calvert et al., 2015; Morford and Emerson, 1999; Scholz et al., 2011). Such a comparison has previously been carried out for the Mexican Margin (Nameroff et al., 2004), where it was found that V was at crustal levels for sediments with BW oxygen concentration >10 µM. When applying the crustal value as baseline for sediments with similar BW O_2 contents from the Northeastern Pacific, the North African Margin, the Arabian Sea (Morford and Emerson, 1999), and the California Margin (Shaw et al., 1990), all samples are within error of crustal background levels (Figure 2). Based on these considerations, it must be concluded that suboxic sediments do not represent a significant marine input or output flux for V. This conclusion does not negate the fact that sediment porewaters rich in V can be released from suboxic sediments (Emerson and Huested, 1991; Morford and Emerson, 1999; Morford et al., 2005; Shaw et al., 1990). However, these fluxes of V were likely initially removed from the water column via either adsorption to oxides or diffusive sequestration by sedimentary organic matter. Hence, the net marine flux for sediments deposited under an oxygenated water column with <3 cm oxygen penetration is likely negligible.

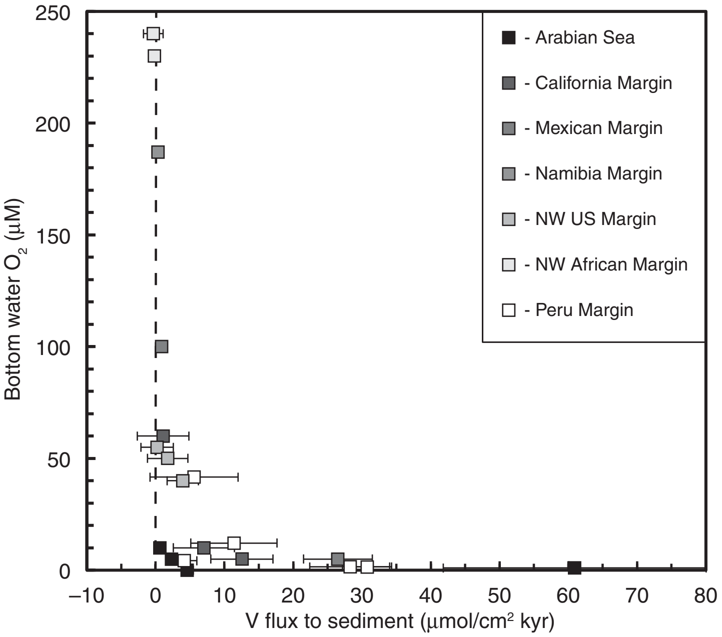

Figure 2 Fluxes of V into organic-rich sediments deposited on continental margins plotted against bottom water oxygen concentrations. Data are tabulated in Table 1.

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In contrast to oxic portions of continental margins, several studies have shown that sediments deposited with BW oxygen concentrations <10 μM are significantly enriched relative to crustal backgrounds (Table 1). Here, sediment core top data are compiled from 10 sites in the Arabian Sea, the Mexican Margin, the Peru Margin, and the California Margin, and we calculate authigenic V fluxes based on V/Al enrichments relative to crustal values (Table 1). Although the range of calculated fluxes is large (2.4–60.9 μmol/cm^2 × kyr), it is notable that every site exhibits a positive V flux (Figure 2) with an average value of 18.8 ± 11.5 μmol/cm^2 × kyr (2se). When this average flux is combined with the global area of open ocean sediment deposition where the sediment–water interface has <9 μM O_2 (764,000 km^2, or 0.21 percent of total seafloor (Helly and Levin, 2004)), the V flux into anoxic sediments is 144 ± 88 Mmol/yr. This estimate is larger but still within error of previous estimates of anoxic V mass fluxes (Emerson and Huested, 1991; Morford and Emerson, 1999). However, in this estimate a specific limit for the amount of oxygen present at the sediment–water interface is used, which is based on published core top V fluxes. Thus, it should be more straightforward in the future to revise this estimate if additional V flux data become available.

Euxinic sediment fluxes are more complex to determine for several reasons. First, some euxinic basins (e.g. the Black Sea) are highly restricted, which may result in lower depositional rates than euxinic basins that are better connected to the open ocean (Lyons et al., 2009). In addition, a significant fraction of the V in highly restricted basins likely originates from local continental runoff rather than from open ocean seawater. These considerations make it difficult to assess the exact area of euxinic sediment deposition that is not affected by basinal restriction. One previous study suggested a best estimate of ~180,000 km^2 (or 0.05 percent of total seafloor (Scott et al., 2008)), but this estimate also included the most reducing portions of OMZs, which have here been included in the estimate for anoxic sediments. That area should, therefore, be considered an upper limit. Deposition rates of V in euxinic sediments are not very abundant, but a single value from the Cariaco Basin yields a flux of ~22 μmol/cm^2 × kyr (Piper and Dean, 2002). This value is similar to what is found for anoxic sediments, which is consistent with the conclusion that marine particles settling in both anoxic and euxinic environments are similarly enriched (Calvert et al., 2015; Ho et al., 2018). If the V flux is combined with the maximum euxinic seafloor area, then a maximum V flux associated with euxinic sediments of 39 Mmol/yr is obtained. However, the true value is likely substantially lower than this, given that the area of truly euxinic seafloor where the water column contains sulfide is likely much lower than what is used here.

Table 1 Authigenic V fluxes calculated for core top continental margi

Sediment core top	Location	BW O$_2$ (μ M)	Al$^{\wedge}$ (μ g/g)	V (μ g/g)	V/Al (×10^{-3})	Percent enrichm rel. CC*
TN047-20	Arabian Sea	0	17,100	43.2	2.53	112.3
NH01 G6 C-47	Santa Barbara Basin, California Margin	1	85,900	150	1.75	46.8
MUC29	Peru Margin	<1.5	39,300	106	2.70	94.0
MUC19	Peru Margin	<1.5	22,300	227	10.2	632.3
MUC39	Peru Margin	4.2	29,100	52.2	1.79	29.1
TN047-22	Arabian Sea	≥5	18,100	33.3	1.84	54.6
NH15P	Mexican Margin	5	79,000	200	2.53	112.8
SPC	Santa Monica Basin, California Margin	5	74,400	123	1.65	38.6
SCR-44	Santa Cruz Basin, California Margin	10	85,600	121	1.41	18.8
TN047-30	Arabian Sea	≥10	10,200	15.2	1.49	25.3
MUC25	Peru Margin	12.1	35,500	60.3	1.70	22.2
2MC39	NW US Margin	40	54,000	104	1.93	20.8
MUC53	Peru Margin	41.6	42,100	64.1	1.52	9.5
WEC213	NW US Margin	50	73,700	125	1.70	6.4

Table 1 (cont.)

Sediment core top	**Location**	**BW O_2 (μ M)**	**Al[^] (μ g/g)**	**V (μ g/g)**	**V/Al ($\times 10^{-3}$)**	**Percent enrichm rel. CC[*]**
4MC33	NW US Margin	55	82,600	133	1.61	1.0
BC6	San Clemente Basin, California Margin	60	83,600	103	1.22	2.9
NH22-P	Mexican Margin	100	72,000	95.0	1.32	10.9
8470–1	Cape Basin, Namibia	187	10,800	15.0	1.39	16.7
3BC8-1	NW African Margin	230	79,000	90.1	1.14	−4.1
1BC1-2	NW African Margin	240	62,000	72.0	1.16	−2.4
PL07-39PC	*Cariaco Basin*	*eux*	*109,600*	*190*	*1.73*	*45.7*

Sediment core from Cariaco Basin in italic to denote deposition in euxinic environment.

[^] Al concentrations in California Margin sediments calculated assuming upper continental crust Al/Ti = 21.2

[*] Upper continental crust (CC) value taken from Rudnick and Gao (2003) except for NW US Margin, where se used (Morford and Emerson, 1999), and Peru Margin, where average Andean andesite is used (Scholz et al.,

[#] Sediment mass accumulation rates (MAR) either as reported or calculated from depositional rates using dens Morford and Emerson (1999). Rates listed for TN047-22 and TN047-30 are assumed identical to TN047-20.

[$] Error bars calculated assuming 10 percent total propagated uncertainty on the sedimentation rates and the A

References 1: (Morford and Emerson, 1999); 2: (Zheng et al., 2000); 3: (Wu et al., 2020); 4: (Scholz et al., 201 1990); 7: (Morford et al., 2005); 8: (Riedinger et al., 2006); 9: (Piper and Dean, 2002).