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Proto-Pacific-margin source for the Ordovician turbidite submarine fan, Lachlan Orogen, southeast Australia: geochemical constraints

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Abstract

The Early Palaeozoic proto-Pacific margin of Gondwana was characterised by a huge turbidite submarine fan with abundant clastic detritus derived from unknown sources within Gondwana. These deposits are widespread in the Lachlan Orogen of southeast Australia and include the Ordovician Adaminaby Group. Here we show that the mudstones and sandstones of the Adaminaby Group have chemical compositions that indicate the detritus in them was derived from a felsic, continental source similar in composition to Post Archean Australian Shales (PAAS). Chondrite normalised REE patterns showing LREE enrichment, flat PAAS normalised patterns and elemental ratios La/Sc, Cr/Th, Cr/V, Th/Sc and Th/U, have been used to support this interpretation. The dominance of quartz, and to a lesser degree plagioclase and biotite in the sandstones, suggests that the source was mainly granodioritic to tonalitic in composition. Th/Yb and Ta/Yb ratios indicate that the source was probably calc-alkaline, continental and shoshonitic. In addition, the presence of detrital muscovite, low-grade metamorphic and felsic volcanic clasts, demonstrates that a low-grade metamorphic terrane and volcanic arc contributed to the detritus observed in the samples. The presence of well-rounded zircons and tourmalines, very high Zr contents, high Zr/Sc and higher Cr/V ratios in some samples particularly in the Shoalhaven River area, indicate that some of the detritus was recycled. SiO₂ versus (Al₂O₃ + K₂O + Na₂O) plots suggest the source areas experienced conditions varying from humid/semi-humid to semi-arid. Textural features and weathering trends of samples from all locations follow a curved pathway on Al₂O₃ - (CaO* + Na₂O) - K₂O (ACNK) diagrams, and indicate that the clays formed from weathering had been K-metasomatised prior to penetrative deformation. Chemical indices of alteration (CIA) reveal that even the freshest sandstones are altered and others are moderately to strongly altered. Discrimination diagrams involving major, trace and REE strongly support a collisional/continental volcanic arc setting that was substantially eroded to produce the plutonic detritus observed in the sandstones. The collisional setting accords with that proposed previously by other authors who suggested that it developed during the Delamerian Orogeny, resulting in the uplifted source areas providing detritus that inundated the backarc and forearc sites of the Macquarie Arc. Some of the detritus, however, may have been derived from a continental arc that existed in the late Cambrian along the margin of the Ross Orogen. Based on palaeocurrent analyses in previous studies and shoshonitic signature of the detritus, it is proposed that the Cambrian volcanics along the eastern active margin of Gondwana provided much of the detritus in the Adaminaby Group. Zircons with the Grenvillian signature suggest that some detritus were also derived from the Ross Orogen.

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Proto-Pacific-margin source for the Ordovician turbidite submarine fan, Lachlan Orogen, southeast Australia: geochemical constraints

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Abstract

The Early Palaeozoic proto-Pacific Pacific margin of Gondwana was characterised by a huge turbidite submarine fan with abundant clastic detritus derived from unknown sources within Gondwana. These deposits are widespread in the Lachlan Orogen of southeast Australia and include the Ordovician Adaminaby Group. Here we show that the mudstones and sandstones of the Adaminaby Group have chemical compositions that indicate the detritus in them was derived from a felsic, continental source similar in composition to Post Archean Australian Shales (PAAS). Chondrite normalised REE patterns showing LREE enrichment, flat PAAS normalised patterns and elemental ratios La/Sc, Cr/Th, Cr/V, Th/Sc and Th/U, have been used to support this interpretation. The dominance of quartz, and to a lesser degree plagioclase and biotite in the sandstones, suggests that the source was mainly granodioritic to tonalitic in composition. Th/Yb and Ta/Yb ratios indicate that the source was probably calc-alkaline, continental and shoshonitic. In addition, the presence of detrital muscovite, low-grade metamorphic and felsic volcanic clasts, demonstrates that a low-grade metamorphic terrane and volcanic arc contributed to the detritus observed in the samples. The presence of well-rounded zircons and tourmalines, very high Zr contents, high Zr/Sc and higher Cr/V ratios in some samples particularly in the Shoalhaven River area, indicate that some of the detritus was recycled.

SiO₂ versus (Al₂O₃+K₂O+Na₂O) plots suggest the source areas experienced conditions varying from humid/semi-humid to semi-arid. Textural features and weathering trends of samples from all locations follow a curved pathway on Al₂O₃ – (CaO*+Na₂O) – K₂O (ACNK) diagrams, and indicate that the clays formed from weathering had been K-metasomatised prior to penetrative deformation. Chemical indices of alteration (CIA) reveal that even the freshest sandstones are altered and others are moderately to strongly altered.

Discrimination diagrams involving major, trace and REE strongly support a collisional/continental volcanic arc setting that was substantially eroded to produce the plutonic detritus observed in the sandstones. The collisional setting accords with that proposed previously by other authors who suggested that it developed during the Delamerian Orogeny, resulting in the uplifted source areas providing detritus that inundated the backarc and forearc sites of the Macquarie Arc. Some of the detritus, however, may have been derived from a continental arc that existed in the late Cambrian along the margin of the Ross Orogen. Based on palaeocurrent analyses in previous studies and shoshonitic signature of the detritus, it is proposed that the Cambrian volcanics along the eastern active margin of Gondwana provided much of the detritus in the Adaminaby Group. Zircons with the Grenvillian signature suggest that some detritus were also derived from the Ross Orogen.

Keywords: Tasmanides, Lachlan Orogen, Adaminaby Group, turbidite, provenance, sediment, geochemistry

1. Introduction

In modern sedimentary systems, the provenance of major submarine fans is readily related to large-scale topography, such as for example the Bengal Fan, which is sourced from the Indian-Eurasian collision zone in the Himalayan-Tibetan orogenic belt (Curry et al., 2003). In ancient systems the reconstruction of sedimentary basins and recognition of source regions is much more dependent on the characteristics of the sedimentary components within the system itself. This is because the large-scale topography has to be inferred from palaeogeographic elements, that may have been either completely or partially removed by erosion or overlain by younger successions. Petrographic data from sandstones have been widely used in determining provenance along with other tools such as palaeocurrent indicators, geochemistry, isotope geochemistry and geochronology, particularly detrital zircon age data but also including Ar/Ar ages of detrital micas and amphibole (Dickinson and Suczek, 1979; McLennan et al., 1993; Weltje and von Eynatten, 2004). Many of these types of analyses have been used to determine the provenance of the major Ordovician turbidite fan in the Lachlan Orogen of southeastern Australia (Turner et al., 1996; Fergusson and Tye, 1999; Fergusson et al., 2013) (Figs. 1, 2).

These turbidites dominate much of the bedrock geology of the Lachlan Orogen and their extent and thickness in the undeformed state has been considered comparable with the Bengal

Fan in the northeastern Indian Ocean (Fergusson and Coney, 1991, 1992; VandenBerg and Stewart, 1992; Fergusson, 2003, 2009). Petrographic studies have highlighted the quartz-rich nature of sandstones in the succession with most samples plotting in the recycled orogen field on a triangular quartz-feldspar-lithic fragment (QFL) plot (Colquhoun et al., 1999; Fergusson and Tye, 1999). Common minor components in these sandstones are low-grade metamorphic rock fragments and detrital micas. Palaeocurrent data from the quartz-rich Ordovician turbidites indicate that the source region was to the south, southwest and west in the Delamerian Orogen of southeastern South Australia, western New South Wales and western Victoria (Powell, 1984; Fergusson and Tye, 1999). $^{40}\text{Ar}/^{39}\text{Ar}$ data on detrital muscovite grains indicate ages of 512 to 480 Ma, in agreement with the timing of the peak of the Delamerian Orogeny (Turner et al., 1996; Foden et al., 2006). An orogenic event of similar age (520-490 Ma) occurred in the Wilson Terrane, Antarctica (Münker and Crawford, 2000).

However, it has been found that the Ordovician turbidites have a consistent detrital zircon age signature with abundant ages in the range 650-500 Ma and lesser but persistent ages in the range 1300-1000 Ma. Both are consistent with a Gondwana source (Veevers, 2000; Veevers et al., 2006). It has been argued that this source is represented by the central Gondwanan orogenic belt formed by collision of West and East Gondwana (Maidment et al., 2007; Williams and Pulford, 2008) and referred to as the “Transgondwanan Supermountain” (Squire et al., 2006). Alternatively, a source has been proposed closer to the site of deposition in the ice-covered hinterland of East Antarctica, and therefore not directly observable (Veevers and Saeed, 2008, 2011).

It is clear that further studies are required to better define the source(s) of the detritus in the sedimentary rocks of the Adaminaby Group and the tectonic setting of the source area. These are the aims of this study and have been achieved by carrying out petrographic and geochemical studies of mudstones and sandstones from several locations in the Lachlan Orogen in southeastern Australia (Fig. 2). Further, geochemical proxies have been used to constrain the climate existing at the time the detritus was being derived from the source rocks. This type of study involving both petrographic and geochemical studies to determine provenance and tectonic setting, has never been carried out on sedimentary rocks of the Adaminaby Group.

2. Geological Setting

The Lachlan Orogen is a major part of the Early Palaeozoic proto-Pacific Gondwana active margin in southeastern Australia (Fig. 1). It consists of rocks of Cambrian to early Carboniferous age whose geological history and tectonic setting has been the subject of much debate in the literature (Foster and Gray, 2000; Glen, 2005; Aitchison and Buckman, 2012; Fergusson et al., 2013). Cambrian rocks of the Lachlan Orogen occur mainly in Victoria, where they include mafic volcanic basement successions with an oceanic forearc and backarc basin magmatic affinity, and in places are overlain by widespread and thick Ordovician turbidites (Crawford et al., 2003; Glen, 2013). Also present in Victoria are the Cambrian sequences of the Glenelg River Complex and Mount Stavely Volcanic Complex that contain calc-alkaline plutonic and volcanic rocks (Crawford et al., 1992; Kemp et al., 2002). In eastern New South Wales, the Ordovician turbidites occur to the west, east and within the Ordovician volcanic and intrusive successions of the Macquarie Arc succession (Fig. 1). These rocks include calc-alkaline shoshonitic lavas and intrusions with arc-type geochemistry (Crawford et al., 2007). Ordovician turbidites east and south of the Macquarie Arc are known as the Adaminaby Group and consists of a lower part dominated by sandy turbidite facies with thin intervals of bedded chert and an upper part with a thick unit (300-400 m) of black shale largely lacking sandstone (VandenBerg et al., 2000; Percival et al., 2011; Bruce and Percival, 2014). A major orogenic event in the late Ordovician to mid Silurian, the Benambran Orogeny, resulted in substantial shortening, crustal thickening and calc-alkaline continental arc volcanism (Collins, 2002). However, the tectonic setting in which the turbidites were deposited is much debated, with models involving multiple subduction zones, along strike terrane translations, island arc - passive margin collision, and a complex backarc setting with anomalous mafic volcanism being proposed (Foster and Gray, 2000; Glen et al., 2009; Aitchison and Buckman, 2012; Quinn et al., 2014).

3. Methods

Sandstones and mudstones of early to late Ordovician age were collected from west of Batemans Bay (Prendergast et al., 2012), Howqua River, Sandy and Merrijig Creeks in the southern Tabberabbera Zone, Shoalhaven River, (Fergusson and Tye, 1999) (Figs. 2, 3).

3.1 Chemical analysis

Sandstones and mudstones were ground to powders in a Tema mill with a chrome steel crusher. All analyses were done on fused discs made from the rock powders. Major, trace and

rare earth elements were determined by Genalysis Laboratory Services, Adelaide using ICP-OES and ICP-MS respectively; loss on ignition (LOI) was determined from 1 g of sample heated at 1050°C. Analytical precision, reproducibility and detection limits are presented in Table A1 and chemical analyses in Table A2.

3.2 *Petrographic analysis*

One hundred and three thin sections of moderately to strongly deformed, fine to coarse grained sandstones of varying grade (subgreenschist to amphibolite facies) from different locations in New South Wales and from the Tabberabbera Zone, in Victoria, were examined using a Zeiss Axioplan Research microscope. Observations on grain shape, mineral content and types of rock fragments were then compared with the petrographic descriptions of other authors (Colquhoun et al., 1999; Fergusson and Tye, 1999), and more importantly used to ascertain variability in the detrital assemblages from location to location and thus provide information on the source rocks responsible for the detrital assemblages.

3.3 *Multi-dimensional discrimination diagrams*

The IgRoCS program of Verma and Rivera-Gómez (2013) was used to identify magma types and to carry out readjustment of major elements on an anhydrous basis. The TecDIA program for acid rocks (Verma et al., 2015) was then used to calculate the discriminant function equations DF1 and DF2 that are required to plot the rock samples on recent discrimination diagrams published by Verma et al. (2012, 2013) for felsic igneous magma; Verma and Armstrong-Altrin (2013) diagrams were used for siliciclastic sedimentary rocks.

4. Results

4.1 *Petrographic studies*

According to McLennan et al. (1993), petrographic analysis is only useful for coarser grained rocks (>1 mm). We agree, because we are aware that detritus in finer grained rocks may not be truly representative of the source area because of sorting. Nevertheless, we have been able to obtain valuable information relating to provenance from fine-grained sandstones by identifying the detrital phases in the samples.

The dominant detrital phases in the sandstones and mudstones are monocrystalline quartz, plagioclase, muscovite, biotite and low grade metamorphic rocks (Table A3); biotite and

muscovite are more common in mudstones. Less common are felsic and intermediate volcanic rocks, polycrystalline quartz and opaque minerals; K-feldspar is rare. In most samples, subrounded to well-rounded zircons and less commonly euhedral, zoned zircons were observed (Fig. A1). Well-rounded zircons are particularly common in the samples from the Shoalhaven River area. Both subhedral and rounded tourmaline grains are also present and a few tourmaline grains exhibit an internal fabric (Fig. A1). Present in a few quartz grains is “Venus Hair” (very fine grained rutile) and some samples have coarse composite quartz grains containing either biotite, muscovite or plagioclase crystals. Although K-feldspar is rare in the samples examined in this study, moderately high contents have been reported in the Pinnak Sandstone (Morand et al., 2005). Felsic volcanic clasts are particularly common in the early Ordovician sandstones at Batemans Bay and the Howqua River (Table A3).

4.2 *Geochemistry*

Chemical analyses of the sandstones and mudstones from the Adaminaby Group are shown in Table A2. These analyses and those from the Snowy Mountains presented by Wyborn and Chappell (1983) have been used to determine the possible rock types that have been eroded to produce the detritus in the sediments, their composition, provenance and tectonic setting of the source region.

Zr/TiO₂ and Nb/Y ratios of most sandstones indicate that they contain detritus that has been derived from a rhyodacitic/dacitic source (Winchester and Floyd, 1977). Only those from the Snowy Mountains and Shoalhaven River areas have samples with either an andesitic or rhyolitic signature (Fig. 4). Chondrite normalised patterns of the sandstones and mudstones (Fig. 5) are similar and have LREE-enriched (La/Yb)_N = 6.24-14.8) and flat HREE patterns. (La/Yb)_N ratios, and total REE contents are higher in the mudstones from Adaminaby than those from Batemans Bay (Fig. 5). Eu depletion is common and Ce fractionation is only apparent in the mudstones from Adaminaby (Fig. 3). Sample HQ5 from Howqua River shows an unusual enrichment in Dy and Er, and sample CCL20 from Adaminaby that is quartz-rich (SiO₂ = 90.74%), much lower REE contents (Fig. 5B). Tm enrichment is apparent in a single mudstone sample (CCL31).

Post Archean Australian Shale (PAAS) normalised patterns (Fig. 6) are flat and exhibit only slightly lower LREE contents than HREE contents, in most samples. Overall, mudstones show greater enrichment in REE than PAAS. Ce, Dy, Er and Tm fractionation is also apparent.

N-MORB normalised patterns for both the sandstone and mudstone samples are similar (Fig. 7). They exhibit Nb, and Ta depletion and high contents of Th (Pearce, 1983). Other features include: (1) Sr depletion, (2) Zr and Hf contents exceeding Nb and Ta in samples containing abundant detrital zircon, and (3) with the exception of Zr and Hf, contents of other elements are higher in the mudstones than sandstones.

5. Discussion

5.1 Geochemistry

Certain trace elements are useful for highlighting compositional differences between samples and possible sources (Ryan and Williams, 2007). However, they can only be used in this way if one particular source area dominates. This appears to be the situation with the sediments from the Adaminaby Group.

As indicated previously, the Zr/TiO_2 and Nb/Y ratios of most sandstones contain detritus derived from a source with a rhyodacitic/dacitic composition. Confirmation that the source has this composition is provided by the samples close to or on the source rock variation line on the Th/Sc versus Zr/Sc plot (Fig. 8). The source rocks have a calc-alkaline magmatic affinity according to the Zr-Y, La-Yb and Th-Yb diagrams of Ross and Bédard (2009;). The LREE enriched and flat HREE chondrite normalised REE patterns support this interpretation, as do the N-MORB normalised patterns because they show features characteristic of calc-alkaline, continental arc rocks, namely, Nb, and Ta depletion, Zr and Hf < Nb and Ta, and high contents of Th (Pearce, 1983) (Figs. 5, 7).

Further, the chondrite normalised REE patterns obtained from mudstones of the Adaminaby Group (Fig. 5), show features typical of clays derived from old continent and fractionated volcanic arc settings (McLennan, 1989; McLennan et al., 1990). Variations in $(La/Yb)_N$ ratios of the mudstones and sandstones indicate that rock types of different composition were eroded in the source area. This is particularly apparent in the Adaminaby area where mudstone units have higher $(La/Yb)_N$ ratios than elsewhere. The depletion in Eu suggests possible plagioclase fractionation in the source rocks and depletion in Ce observed in some mudstones that the clays from which they were formed have interacted with oxic seawater resulting in a change in valence state from Ce^{III} to Ce^{IV} (Wilde et al., 1996).

That a continental source provided the detritus is supported by La/Sc (1.78-5.18), Th/Sc (0.71-2.99) ratios (UCC - La/Sc = 2.21; Th/Sc = 0.75; Rudnick and Gao, 2003) (Table A2),

flat, PAAS normalised patterns (Fig. 6), low ϵ_{Nd} values (-10.8 to -11.1; Turner et al., 1993), N-MORB normalised patterns and Th/Yb and Ta/Yb ratios. The latter indicate the detritus was derived from an active continental arc margin and possibly had a shoshonitic affinity because Ta/Yb ratios are high (Gorton and Schandl, 2000) (Fig. 9).

Cr/Th ratios for most sandstones range from 1.86 to 7.16 and indicate source rocks of silicic composition with very little influence of mafic rocks (Condie and Wronkiewicz, 1990) (Table A2). Confirmation of the latter is shown by the lack of mafic clasts in the sandstones. However, two late Ordovician sandstones from the Shoalhaven River area (samples 16379; 16359; Fergusson and Tye, 1999) have much higher Cr/Th ratios (Table A2). These have a higher content of lithic clasts (Fergusson and Tye, 1999) and opaque minerals both of which may have been responsible for the higher Cr content.

Al_2O_3/TiO_2 ratios of clastic rocks are considered to be essentially identical to source rocks (Hayashi et al., 1997). Based on this assumption, Al_2O_3/TiO_2 ratios have been calculated for all samples and an Al_2O_3 versus TiO_2 diagram created to ascertain possible sources for the samples from the Adaminaby Group (Table A2, Fig.10). The results have been compared to those of Bruce and Percival (2014) that were obtained from cherts associated with the sediments of the Adaminaby Group and that were used to determine the type of detrital input. The ratios reveal that the presence of a slightly more mafic source than Post-Archean Australian Shale (PAAS; $Al_2O_3/TiO_2 = 19.9$; Taylor and McLennan, 1985) and Upper Continental Crust (UCC; $Al_2O_3/TiO_2 = 24$; Rudnick and Goa, 2003) with the most mafic influence recorded in the sandstones from the late Ordovician Shoalhaven River samples (Range 13-20; $n = 9$; $x = 15$). This is in contrast to Bruce and Percival (2014) who noted the detrital input changed from PAAS to Upper Continental Crust from the early to mid-Ordovician, indicating a change to a more felsic source with time.

Higher contents of V and Sc are present in the mudstones than in the sandstones, higher than in Upper Continental Crust ($V = 97$; $Sc = 14$; Rudnick and Goa, 2003). This occurs because they are fractionated into the clays and elements such as Cr in chromite and Zr in zircon go into sands during transportation and deposition (McLennan et al., 1993). The enrichment of these elements in all of the samples may also be due to the leaching out of the alkali/alkali earth elements during weathering of the source rocks. The higher V and Sc contents suggest the presence of a mafic component albeit minor in the sandstones and mudstones. The source of the mafic elements is not known but could be from a mafic-ultramafic source. Such a

source may be the ultramafic – mafic complexes of Cambrian age known to occur in the Dundas Trough in western Tasmania (Crawford et al., 1992) but other sources along the proto-Pacific margin of Gondwana may have contributed.

5.2 *Cycling and recycling*

The petrographic studies we have carried out suggest that major recycling has not taken place because, in the less deformed rocks, detrital quartz and plagioclase are consistently angular to subrounded, and rounded quartz grains are relatively uncommon. Biotite also reflects this lack of recycling because it is only slightly degraded in many samples and still retains its pleochroism; others are relatively altered, commonly to chlorite. These features show that the biotite had experienced one sedimentary cycle and has not been subjected to substantial chemical weathering. By contrast, well rounded tourmaline and in particular, igneous and metamorphic zircons that dominate over euhedral zircons, have been noted in samples from the Adaminaby Group (Fergusson and Fanning, 2002; Fergusson et al., 2013) and in the present study (Table), indicating substantial sedimentary transport and recycling. This is substantiated by Th/Sc and Zr/Sc ratios of the psammitic rocks most of which record high Zr/Sc ratios, particularly in samples from the Shoalhaven River area (Fig. 8). The higher ratios are due to the concentration of zircon brought about by sedimentary sorting and recycling (McLennan et al., 1993). Significantly, in samples with high Zr contents such as those in the Shoalhaven River area (>300 ppm), slightly higher Cr/V ratios are recorded. This suggests that a Cr-bearing mineral such as chromite has been concentrated synchronously with the zircon in these samples. This is supported by the rare occurrence of chromite in reworked turbidites interpreted as contourites (Jones et al., 1993). The presence of rounded and euhedral zircons, rounded tourmaline and quartz, and possibly chromite is evidence for at least two possible source regions.

An additional feature of Figure 8 is that the pathway defined by the samples intersects the source rock variation pathway close to granodiorite, confirming our petrographic and geochemical conclusions based on the composition of the sandstones and mudstones, that felsic rocks dominate the source region.

5.3 *Weathering and climate*

To evaluate the degree of weathering of the psammitic rocks from the different locations, Chemical Index of Alteration (CIA) values have been determined and the chemical

composition of the samples plotted on an A-CN-K diagram ($A = \text{Al}_2\text{O}_3$; $C = \text{CaO}^*$; $N = \text{Na}_2\text{O}$; $K = \text{K}_2\text{O}$; Nesbitt and Young, 1984). CIA is the most accepted of the available weathering indices according to Bahlburg and Dobrzinski (2011) and is expressed as $\text{CIA} = \text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO}^*)$ using molecular proportions; CaO^* represents Ca in silicates.

The CIA values range from 58 to 82 for the sandstones and 75 to 79 for the mudstones (Fig. 11). However, the pathway defined by the samples on the A-CN-K diagram is curved and intersect the A-K tie line at the illite-muscovite compositional field and the feldspar join at approximately average granodiorite (Batemans Bay; Howqua River; Adaminaby; Fig. 11A,C,D) and average granite for the Snowy Mountains region (Fig. 11B). The curvature in the pathway implies that the samples have been K-metasomatised prior to deformation because the pathway of alteration should be parallel to the A-CN boundary (Nesbitt and Young, 1984; Fedo et al., 1995). Evidence for this metasomatism can be observed in less deformed samples with high CIA, in the form of extensive replacement of lithic clasts and plagioclase grains by unorientated, fine grained white mica (illite?). Well developed cleavage defined by muscovite wraps around these clasts and grains indicating that alteration occurred prior to penetrative deformation. To correct for this alteration, procedures discussed in Fedo et al. (1995) have been used to determine the palaeoweathering indices prior to metasomatism. The CIA values range from 59 to 85 for the sandstones (Fig. 11). The greater loss of alkali/alkaline earths experienced by the mudstones during weathering results in higher CIA values of 77 to 88 for them.

The environment in which the weathering of the source rocks took place has been determined from the diagram of Suttner and Dutta (1986) that separates samples formed in arid and humid environments on the basis of their SiO_2 and $(\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O})$ contents (Fig. 12). It shows that both arid and humid conditions are recorded by the samples from the Adaminaby Group with some from the Snowy Mountains region and the Sandy and Merrijig creeks area, exhibiting the greatest chemical maturity (Fig. 12). Those samples plotting in the Arid area have compositions reflecting semi-arid conditions according to the studies of Suttner and Dutta (1986). They show a substantial reduction in chemical weathering and occur in all sampled locations.

Support for humid conditions is suggested by: (1) palaeomagnetic data that shows the Australian continent lay in low latitudes during the Ordovician (Embleton, 1984; Torsvik and

Cocks, 2013) and (2) quartz-feldspar-rock (Q-F-R) values determined by Colquhoun et al. (1999) and Fergusson and Tye (1999) from early to late Ordovician sandstones in the Howqua River, Shoalhaven River, Sandy-Merrijig Creeks and Mudgee areas. Examination of the Q-F-R ratios of the sandstones that were analysed in previous studies, reveal that warm-semi-arid conditions prevailed during the earliest Ordovician and temperate humid conditions subsequently, according to the Q-F-R ratios suggested by Suttner and Dutta (1986).

5.4 Tectonic setting

Several discrimination diagrams have been used widely to determine the tectonic setting from the geochemistry of mudstones and sandstones (e.g., Bhatia, 1983; Bhatia and Crook, 1986; Roser and Korsch, 1986). However, studies by Ryan and Williams (2007) and Verma and Armstrong-Altrin (2013) showed that these diagrams must be used with caution, are only moderately successful in determining tectonic setting, and cannot be applied universally. Further, Floyd et al. (1991) have also pointed out that sedimentary sequences can include detritus derived from a number of geologically unrelated tectonic settings, and thus the geochemical signatures may be complex. Despite these problems, new multi-dimensional diagrams have been devised for siliciclastic sediments that successfully discriminate between tectonic settings and show that alteration, sediment transport, sorting or post-depositional processes do not affect the discrimination (Verma and Armstrong-Altrin, 2013; Verma et al., 2013). Therefore, to avoid making incorrect interpretations of the geochemical data obtained from the Adaminaby Group sedimentary rocks to determine setting, the discrimination diagrams of Verma et al. (2013) have been used. The tectonic settings suggested by these diagrams have been compared with those of Thiéblemont (1999) and Verma et al. (2013) for felsic magmatic rocks because much of the detritus has been derived from felsic rocks. We believe it is valid to use these discrimination diagrams because both the sandstones and mudstones have strikingly similar patterns (Figs. 5-7, 9), which suggest a similar provenance prevailed to produce all the detritus observed in the sediments. The diagram of Thiéblemont (1999) has been successfully used to discriminate subduction-related and mantle-derived calc-alkaline arc rocks in the Western Cordillera of the Andes from those of crustal magmatic origin developed in the Altiplano-Puna, a site of intense volcanism of calc-alkaline, shoshonitic affinity and thick crust (70 km). The $(\text{Nb/Zr})_N$ versus Zr plots of Thiéblemont (1999) supports the continental origin of the sediments in the Adaminaby Group and importantly shows that the detritus has been derived from a source that is “collision” rather than subduction related (Fig. 13). A collisional setting is confirmed by the discriminant-

function multidimensional diagram for high-silica clastic sediments of Verma and Armstrong-Altrin (2013), based on major element data (Fig. 14). It reveals that most samples from the Adaminaby Group plot in the Collision and less commonly in the Continental Rift and Arc fields. However, the ACNK plots discussed previously (Fig. 11) indicate that K-metasomatism may have affected the samples (see previous discussion), thus settings based on major elements must be treated with caution, even though modelling has been able to show that sample position does not change significantly with changes in any of the elements (Verma and Armstrong-Altrin, 2013). To avoid problems that may arise from the use of major elements, we have chosen the tectonic settings derived from granitic rocks based on immobile elements only, assuming that similar results will be obtained from siliciclastic sediments as granitic rocks. These diagrams suggest collision and continental arc settings, the former shown more commonly by the mudstones of the Adaminaby Group (Fig. 15). Significantly, the samples follow linear trends in some of the diagrams that define a transition from one setting to another, implying that the setting may have changed with time (Fig. 15C). Similar trends have been noted by Verma et al. (2012) for rocks from the Adamello Massif in northern Italy. Some evidence for this change in setting is apparent in the QmFLt diagram of Fergusson and Tye (1999) that show a few of their samples plotted in the dissected arc (DA) field, the majority in the quartzose and transitional recycled fields. As will be discussed later, it is more likely that the discrimination diagrams indicate two different tectonic settings from which the detritus was derived.

The settings suggested by these discrimination diagrams are confirmed by the chondrite normalised REE patterns that show LREE enrichment, N-MORB normalised patterns that are typical of active continental margins and Th/Yb and Ta/Yb ratios (Pearce, 1983; Gordon and Schandl, 2000) (Figs. 5, 7, 9). The collisional setting suggested by the geochemistry (Figs. 14, 15) can be reconciled with the recycled orogen setting proposed by Colquhoun et al. (1999) and Fergusson and Tye (1999), based on modal analyses of sandstones, because such orogens can be formed by continent-continent collision or island arc-continent collision. Further, the high quartz/feldspar ratios, abundance of meta-sedimentary lithic fragments and lack of volcanic clasts in most sandstones from the Adaminaby Group, noted by Colquhoun et al. (1999) and Fergusson and Tye (1999), support a collisional setting.

5.5 Provenance

This study has shown that most detritus in the rocks from the Adaminaby Group has been derived from a terrane dominated by a felsic, possibly shoshonitic, source. The consistent presence of quartz, plagioclase and biotite in samples from sequences of early to late Ordovician age suggests that this source continued to provide detritus throughout the Ordovician. Previous studies involving modal analyses of sandstones in the Adaminaby Group by Fergusson and Tye (1999) and Colquhoun et al. (1999) have revealed that this detritus has been derived from a recycled orogen, and our studies indicate a collisional setting. However, the discrimination diagrams (Figs. 13-15) also suggest a continental arc setting. This could be a Cambrian continental arc in the Ross Orogen of Antarctica as will be discussed later. Further, U-Pb zircon data also show that a number of geologically unrelated tectonic settings and thus sources have been involved (Turner et al., 1996; Fergusson et al., 2013). Common to most locations, are zircons with Pacific-Gondwana signatures (600-500 Ma) and Grenville-Gondwana signatures (1300-1000 Ma; Fergusson et al., 2013). Those recording 1100-550 Ma ages are rounded and show complex internal structures in contrast to the younger Delamerian zircons that have a euhedral shape (Fergusson et al., 2013). Less common are metamorphic zircons (Fergusson and Fanning, 2002; Fergusson et al., 2005). This study has revealed a minor detrital component consisting of rounded to well-rounded quartz, zircon and tourmaline, suggesting a minor older source contributed detritus derived from sedimentary and igneous sources of probable Grenvillian age.

A second, less common type of detritus observed in the samples has been obtained from a low grade metamorphic terrane that included cherts, fine grained quartz-white mica schists, quartzites, polycrystalline quartz, muscovite, minor meta-siltstone and slate (Table A3). Muscovite, a minor phase in all samples, is probably of metamorphic origin because it is uncommon in granitoids. Rarely, it shows internal fabrics (Si) that supports this interpretation and suggests it has been derived from a low grade metamorphic terrane, a source previously proposed by Fergusson and Tye (1999) and Colquhoun et al. (1999). This terrane appears to be the same source area as that for the felsic plutonic rocks because the same degree of roundness is shown by the plutonic and metamorphic detritus.

Delamerian ages (507-480 Ma) have been obtained from muscovite in rocks from the Adaminaby Group (Turner et al., 1996; Foster et al., 1998; Fergusson and Phillips, 2001) and from detrital, non-rounded zircons (Fergusson et al., 2013) implying that the two source areas may have been coupled. The presence of felsic volcanic clasts noted in the earliest and late Ordovician suggests a third source has been involved, namely a terrane containing

continental arc volcanics. ϵ_{Hf} values obtained by Glen et al. (2011), from zircons varying in age from ~490 to 540 Ma in early Ordovician sediments, are highly negative, suggesting they were derived from an evolved continental arc source at that time. Such an age distribution is widespread and a feature of Ordovician quartzose sandstones from the Lachlan Orogen (Fergusson et al., 2005). This continental signature was also recognised by Bruce and Percival (2014) in early to middle Ordovician cherts of the Girilambone and Adaminaby groups. Thus a continental arc signature is recorded in all types of sedimentary rocks in the Adaminaby Group.

Palaeocurrent analyses of sandstones in the Adaminaby Group indicate sediments came from the southwest to west during the early to middle Ordovician, and south during the late Ordovician (Jones et al., 1993; Fergusson and Tye 1999). Assuming that later events had not rotated the sequences that recorded the palaeocurrent data, the detritus has been derived from terranes to the west and south, containing rocks of Cambro-Ordovician, Delamerian and Grenvillian (1200-1100 Ma) age. Whether these rocks were found in the one terrane or in separate terranes is not clear. Confirmation will only arise if zircons are found with Grenvillian cores and Delamerian rims.

The major source of the Ordovician turbidites appears to be the Delamerian Orogen during the early to middle Ordovician, and the change in palaeocurrent directions and reduced sediment volumes in the late Ordovician indicates a more distal source, possibly East Antarctica adjacent to the Ross Orogen, (Turner et al., 1996; Fergusson and Tye, 1999; Fergusson et al., 2013) (Fig. 1). The most likely candidates in the Delamerian Orogen responsible for the majority of the detritus are the post collisional continental rift rocks in the Mt Stavelly Volcanic Complex and Mount Read Volcanics because they contain medium to high-K calc-alkaline volcanic rocks, less common shoshonites and granodiorites (Crawford et al., 1992, 1996), a feature recognised in the composition of the sandstones and mudstones (Fig. 9). Further, the rocks in the Mt Stavelly Volcanic Complex have a Sr isotopic, Andean type continental signature (Gray and Webb, 1995). However, the proportion of rocks with granodioritic composition in these sequences is limited and unlikely to supply sufficient detritus throughout the Ordovician, thus other sources are required. Possible additional sources could be the Glenelg River Complex that contains abundant low to high K, acid plutonic rocks (Kemp et al., 2002) as well as the volcanic and intrusive rocks of similar age and composition to the Mount Read Volcanics that occur in the Transantarctic Mountains and the Wilson Terrane (Münker and Crawford, 2000; Squire and Wilson, 2005) (Fig. 1).

Veevers et al. (2006) suggest that the zircons in the late Ordovician Bumballa and Sunlight Creek formations (Shoalhaven River area and eastern Victoria, respectively) were derived from an area between Bungar Hills and the Transantarctic Mountains, Antarctica, based on the similarity of ages (Pan-Gondwanaland, 700-500 Ma) obtained from them and from alkaline zircons in the Prydz-Leeuwin Belt. If this was true then it could be expected that zircons in the Ordovician sandstones would reflect the alkaline nature of this belt. This has not been proven because zircons from the Adaminaby Group have not yet been chemically analysed. One possible source of the zircons recording Grenvillian ages (1200-1100 Ma) is the early Cambrian Kanmantoo Group, east of the Gawler Craton, South Australia, because detrital zircon patterns in the sediments from this Group are similar to those recorded in the Lachlan Orogen (Ireland et al., 1998). However, the Kanmantoo Group is associated with Neoproterozoic rocks with detrital zircons of Palaeoproterozoic to Neoproterozoic age and many with a Mesoproterozoic age (Ireland et al., 1998). These are not common in the Ordovician Adaminaby Group. Thus the Kanmantoo Group can be discounted as a possible source of the detrital zircons in the Adaminaby Group. For the moment, unless further studies suggest otherwise, the source of the Grenvillian zircons must be East Antarctica as has been suggested previously by Fergusson et al. (2013).

The less common volcanic clasts and metamorphic detritus could also have been derived from the same source area in the Delamerian Orogen. The latter may have come from the low grade, deformed and metamorphosed Cambrian rocks of the Glenelg River Metamorphic Complex of western Victoria that were juxtaposed against the Mount Stavely Volcanics at the time detritus was being fed into basins offshore from the eastern margin of Gondwana during the Ordovician (Cayley, 2011). The mafic rocks that occur in the sequences above the Mount Read Volcanics and associated with the Mount Stavely Volcanic Complex appear to have contributed little detritus at the time the sandstones were deposited, because Cr/V ratios are notably low in all but the sandstones from the Shoalhaven River area.

In summary, two major sources we believe were responsible for the detritus that fed into the basins offshore from the eastern margin of Gondwana during the Ordovician. An important source were mountain ranges produced by continent-island arc collision and subsequent rifting of the post collisional arc in the Delamerian Orogen. The rocks transported and subsequently uplifted during the collision imposed the continental signature now observed in the sediments. Another source was an active continental arc on the margin of Antarctica during the mid to late Cambrian (515-490 Ma). In this setting, volcanic and plutonic rocks

with continental arc, calc-alkaline affinity that occur in the Wilson terrane and Transarctic Mountains provided much of the detritus (Münker and Crawford, 2000; Squire and Wilson, 2005). Thus the volcanic arcs that arose after the continent-island arc collision and from subduction provided the detritus observed in the samples from the study area. This tectonic scenario is reflected in the discrimination diagrams.

6. Conclusions

This geochemical/petrographic study reveals that the mudstones and sandstones of the Ordovician Adaminaby Group, Lachlan Orogen, were derived from a felsic, continental source. Evidence supporting this interpretation includes LREE enriched chondrite normalised REE patterns, flat, PAAS normalised patterns and La/Sc, Cr/Th, Cr/V, Th/Sc and Th/U ratios. A minor mafic contribution is apparent in only some samples. Quartz and to a lesser degree plagioclase and biotite are common in the sandstones, suggests the main source was mainly granodioritic. Th/Yb and Ta/Yb ratios indicate that these rocks were calc-alkaline, continental and probably shoshonitic. The presence of detrital muscovite, low grade metamorphic and felsic volcanic clasts, indicate that a low grade metamorphic terrane and volcanic arc contributed to the detritus observed in the samples.

The low degree of roundness of most clasts suggests that they have experienced only one cycle of erosion. However, the presence of well-rounded zircon, quartz and tourmaline, very high Zr contents, high Zr/Sc and higher Cr/V ratios in samples particularly in the Shoalhaven area, indicates some of the detritus was recycled.

SiO₂ versus (Al₂O₃+K₂O+Na₂O) plots reveal the source areas experienced conditions varying from humid / semi-humid to semi-arid. Weathering trends of samples from all locations follow a curved pathway on A-CN-K diagrams that intersect the feldspar and join at a point suggesting the source rock was compositionally granodioritic. Chemical indices of alteration (CIA) reveal that even the freshest sandstones are altered and others moderately to strongly altered, particularly those in the Snowy Mountains region.

The detritus observed in the samples appears to have been derived from rocks in a collisional/continental volcanic arc setting. Based on palaeocurrent analyses carried out in previous studies and the calc-alkaline, shoshonitic signature of the detritus, it is proposed that the Mt Stavelly Volcanic Complex and Mt Read Volcanics provided some of the detritus in the Adaminaby Group. However, to account for the all the detritus in the Ordovician

successions, Cambrian volcanics and plutonics along the eastern active margin of Antarctica must also have been a major source.

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Appendix A

Supplementary files

Table A1. Accuracy and precision of analyses, and detection limits.

Table A2. Whole rock analyses of sandstones and mudstones from the Adaminaby Group, southeastern Australia.

Table A3. Detrital phases in sandstones from the Adaminaby Group.

Map. Adaminaby Group (southeastern Australia) – sample locations Google Earth KMZ file.

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Figures

Fig. 1. East Gondwana following the reconstruction of de Wit et al. (1988) but modified after Myers et al. (1996), Gray et al. (2008), Boger (2011) and Torsvik and Cocks (2013). Cratons in Australia and Antarctica are from Myers et al. (1996) and Boger (2011) respectively. The hypothetical source region for the Pacific-Gondwana detrital zircons in the Ordovician turbidites of the Lachlan Orogen is shown in red and is inferred under East Antarctic ice sheet

in the hinterland of the Ross Orogen (see text). Abbreviations: AFMB—Albany–Fraser–Musgrave belt, DO—Delamerian Orogen, GI—Greater India, GSM—Gamburtev Subglacial Mountains, GP—Grunehogna Province, NAC—North Australian Craton, PG—Pacific-Gondwana sediment source, SAC—South Australian Craton, TAO—Terra Australis Orogen, WAC—West Australian Craton.

Fig. 2. Distribution of Ordovician turbidites (Adaminaby Group and equivalents) and volcanic and volcanoclastic rocks of the Macquarie Arc. Locations of the five areas of samples are shown (see supplementary Google Earth kmz file for locations of all samples). Map drawn using ArcGIS software with digital data from Geoscience Australia (2010). See Fig. 1 for location in an early Palaeozoic context.

Fig. 3. Time-space plot showing the context of samples in selected zones of the Lachlan Orogen in the Neoproterozoic to late Ordovician. Also shown are the Delamerian Orogen in South Australia and western Tasmania. Data compiled from the following sources:

Delamerian Orogen in South Australia – Preiss (2000), Foden et al. (2006); Grampians–Stavely Zone – Crawford et al. (2003), Cayley (2011); western Tasmania – Turner et al. (1998); western Stawell Zone – Miller et al. (2005), Squire and Wilson (2005); Tabberabbera Zone – Fergusson and VandenBerg (2003); Bega and Narooma zones – Glen (1994), Prendergast (2007).

Fig. 4. Zr/TiO_2 versus Nb/Y plot of Winchester and Floyd (1977) showing that most sandstones in the Adaminaby Group contain detritus derived from a rhyodacitic/dacitic source.

Fig. 5. Chondrite normalised patterns for samples from A – Batemans Bay; B – Adaminaby; C - Howqua River; D – Shoalhaven River. Note Eu depletion in all patterns, Ce depletion in pelites from Adaminaby, Tm enrichment in sample from Adaminaby, Dy and Er enrichment in HQ5 from Howqua River and lower contents of REE in CCL20 from Adaminaby (empty diamond). Mudstones – filled red circle; sandstones – empty circle. Normalising values are from Sun and McDonough (1989).

Fig. 6. Post-Archean Australian Shale normalised patterns for samples from (A) – Batemans Bay; (B) – Adaminaby; (C)– Howqua River; (D) – Shoalhaven River. Normalising values are from Taylor and McLennan (1985). Note: Ce depletion in mudstones and Tm enrichment in one sample from Adaminaby; Dy and Er enrichment occurs in one sample from Howqua River. Symbols as in Fig. 5.

Fig. 7. N-MORB normalised patterns for samples from (A) – Batemans Bay; (B) – Adaminaby and Howqua River; black diamond – CCL20 – SiO_2 – rich sample ($\text{SiO}_2=90.74$) showing lowering of contents of other elements. (C) – Shoalhaven River and Merrijig Creek. Black square – 16280. Note: Nb, Ta depletion and Th enrichment, features typical of calc-alkaline, continental arc rocks (Pearce 1983). Normalising values from Sun and McDonough (1989). Symbols as in Fig. 5.

Fig. 8. Th/Sc and Zr/Sc ratios of sandstones (diagram after McLennan et al., 1993). Average granite, granodiorite and TTG (tonalite-trondjemite-granodiorite) from Condie (1993). The compositional variation line is defined by sedimentary rocks from active continental margins least affected by sorting and recycling. Note that most sandstones define a pathway suggestive of zircon accumulation and sediment recycling.

Fig. 9. Th/Yb versus Ta/Yb discrimination diagram for intermediate and felsic rocks of Gorton and Schandl (2000). Note all samples from the Adaminaby Group cluster in one location where values for each ratio are high indicating possible medium-high K calc-alkaline-shoshonitic affinity. ACM – active continental margin; WPVZ – within plate volcanic zones; WPB – within plate basalts; MORB – mid ocean ridge basalt. Symbols as in Fig. 5.

Fig. 10. TiO_2 versus Al_2O_3 plot of Schieber (1992) showing that all sandstones from the Adaminaby Group plot on or above Post Archean Australian Shale (PAAS). The PAAS and Upper Continental Crust (UCC) lines are from Taylor and McLennan (1985) and Rudnick and Goa (2003) respectively. Data for granodiorite from Condie (1993). Symbols as in Fig. 5.

Fig. 11. Samples from the Adaminaby Group plotted in terms of $\text{Al}_2\text{O}_3 - (\text{CaO}^* + \text{Na}_2\text{O}) - \text{K}_2\text{O}$ (mol. proportions; A-CN-K). CaO^* represents Ca in silicate-bearing minerals only. Symbols as in Figure 5. Diagram after Nesbitt and Young (1984). (A) – Batemans Bay; (B) – Snowy Mountains; (C) – Adaminaby and Howqua River; (D) – Shoalhaven River and Merrijig Creek. Corrected minimum and maximum values are shown for the sandstones and mudstones in the different locations. Note: samples follow the same curved pathway intersecting the plagioclase – K-feldspar tie line close to granodiorite (2) and the AK boundary at illite. (1) – granite. Composition of granite and granodiorite from Condie (1993). Symbols as in Fig. 5.

Fig. 12. SiO_2 versus $\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O}$ diagram of Suttner and Dutta (1986). Note that most sandstones plot close to Humid-Arid border indicating semi-arid to semi-humid conditions.

Fig. 13. $(\text{Nb}/\text{Zr})_N$ versus Zr diagram of Thiéblemont (1999) showing sandstones and mudstones from all locations. Note that the majority of samples plot in the collision related field. Normalising values from Hofmann (1988). (A) field of subduction related series; (B) calc-alkaline to alkaline collision related lavas and plutons; (C) intraplate felsic lavas and granitoids; (D) peraluminous leucogranites. Note, samples with high recycled zircon contents (>200 ppm) not included. Symbols as in Fig. 5.

Fig. 14. Multi-dimensional, log-ratio major-element based, discriminant-function diagram for high silica clastic sediments (Verma and Armstrong-Altrin, 2013). Settings – arc, continental rift and collision (col).

Fig. 15. Multi-dimensional, log-ratio immobile-element based, discrimination-function (DF1-DF2) diagrams for granites (Verma et al., 2013). IA-Island Arc; CA-continental arc; CR-continental rift; COL-collision; OI-ocean island. Note that sandstones and mudstones plot in continental arc and Collision fields. Symbols as in Fig. 5.

Supplementary Figure A1

Fig. A1. A – photomicrograph of sample 154 showing rounded tourmaline (T), with planar internal fabric, subangular quartz (Q), detrital muscovite (M) and biotite (B) blades, lithic clast (L) and opaque minerals (O). B – photomicrograph of sample 154 showing subrounded zircon (Z), subangular to subrounded quartz (Q), detrital muscovite (M) and biotite (B) blades.

Table A1 Accuracy and precision of analyses and detection limits.

Sample No	Duplicate		International	Standards	Instrument	Detection limits
	P920A	P920A	SY-4 20.75	GSP-2		
Al ₂ O ₃	18.84	18.84	(20.69)	14.68 (14.9) 1331.6	OE	0.02
Ba	184.7	178.3	340 (340)	(1340)	MS	0.5
CaO	2.28	2.28	8.07 (8.05)	2.08 (2.1)	OE	0.02
Ce	149.6	147.8	120.9 (122)	416.3 (410)	MS	0.5
Cr	124	124	X (12)	22 (20)	OE	20
Cs	3.11	2.94	1.54 (1.5)	1.16 (1.2)	MS	0.05
Dy	14.71	15.44	18.95 (18.2)	5.36 (6.1)	MS	0.05
Er	7.11	7.17	14.55 (14.2)	2.03 (2.2)	MS	0.05
Eu	4.48	4.44	2.03 (2)	2.27 (2.3)	MS	0.05
Fe ₂ O ₃	1.16	1.17	6.23 (6.21)	4.84 (4.9)	OE	0.02
Ga	7.4	7.7	36.9 (35)	20.7 (22)	MS	0.1
Gd	20.91	20.73	15.21 (14)	13.99 (12)	MS	0.05
Hf	4.6	2.7	11.2 (10.6)	13.1 (14)	MS	0.1
Ho	2.74	2.83	4.36 (4.3)	0.91 (1)	MS	0.02
K ₂ O	1.2	1.19	1.69 (1.66)	5.22 (5.38)	OE	0.02
La	85.7	84	58.4 (58)	179.6 (180)	MS	0.2
Lu	0.86	0.84	2.1 (2.1)	0.19 (0.23)	MS	0.02
MgO	0.8	0.8	0.53 (0.54)	0.96 (0.96)	OE	0.01
MnO	0.15	0.16	0.11 (0.108)	0.04 (nd)	OE	0.02
Na ₂ O	8.44	8.45	7.14 (7.1)	2.74 (2.78)	OE	0.02
Nb	116	115.5	12.8 (13)	27.3 (27)	MS	0.1
Nd	90.6	90.8	58.9 (57)	200.2 (200)	MS	0.1
Ni	26	26	X (9)	X (17)	OE	20
P ₂ O ₅	1.58	1.6	0.16 (0.13)	0.28 (0.29)	OE	0.01
Pr	20.92	20.83	15.19 (15)	54.98 (51)	MS	0.05
Rb	51.8	53.1	54.8 (55)	246 (245)	MS	0.1
Sc	15	15	X (1.1)	X (6.3)	OE	10
SiO ₂	59.94	59.73	49.92 (49.9)	65.25 (66.6)	OE	0.03
Sm	21.37	21.28	13.2 (12.7)	25.06 (27)	MS	0.05
Sr	690.9	718	1205.3 (1194)	235.6 (240)	MS	0.2
Ta	5.5	5.9	0.7 (0.9)	0.8 (nd)	MS	0.1
Tb	2.59	2.47	2.6 (2.6)	1.13 (nd)	MS	0.02
Th	7.66	7.66	1.32 (1.4)	105.33 (105)	MS	0.05
TiO ₂	3.12	3.12	0.28 (0.287)	0.64 (0.66)	OE	0.02
Tm	0.99	0.99	2.27 (2.3)	0.3 (0.29)	MS	0.05
U	5.5	5.48	0.96 (0.8)	2.41 (2.4)	MS	0.05
V	155	155	X (8)	47 (52)	OE	10
Y	78.7	80.8	120 (119)	25.8 (28)	MS	0.5
Yb	6.14	5.98	15.17 (14.8)	1.35 (1.6)	MS	0.05
Zr	378	375	582 (517)	541 (550)	MS	1
LOI	2.44	2.43			GR	0.01

X - below detection limit;

nd - not determined;

OE - lithium metaborate/tetraborate fusion analysed by inductively coupled plasma optical emission.

MS - lithium metaborate/tetraborate fusion analysed by inductively coupled plasma mass spectrometry.

(20.69) - standard value.