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Geochemistry of coal–bearing Permo–Triassic strata in Allan Hills, South Victoria Land, Antarctica: Implications for palaeoclimate

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ABSTRACT

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Major, trace and rare earth element (REE) geochemistry has been carried out in this paper to characterize source–rock weathering and climatic variability of the late Permian Weller Formation and the late Triassic Lashly Formation of Gondwana sequences which have yielded rich record of plant mega–and micro fossils associated with coal beds in post–glacial conditions in Allan Hills of South Victoria Land, Antarctica. The geochemistry suggests dominantly a felsic provenance with a volcanogenic input and role of weathering and hydrothermal alteration. The palaeoclimatic interpretation derived from geochemical analysis indicates warm, temperate and humid conditions during the late Permian, and warm and humid conditions during the late Triassic.

Key–words—Geochemistry, Permian, Triassic, Allan Hills, Antarctica.

ऐलन पहाड़ियां, दक्षिण विक्टोरिया भूमि, अंटार्कटिका में कोयला–धारक पर्मो–ट्रायसिक स्तरों का भू–रसायनविज्ञानः पुराजलवायु निहितार्थ

संदीप के. पंडिता, एन.एस. सिद्धैया, रजनी तिवारी, शंकर चैटर्जी एवं दीपा अग्निहोत्री

सारांश

गोंडवाना अनुक्रमों के विलंबित पर्मियन वैल्लर शैलसमूह एवं विलंबित ट्राइएसिक लैशली शैलसमूह का स्रोत शैल अपक्षय एवं जलवायवी परिवर्तनीयता को अभिलक्षणित करने के लिए इस शोध पत्र में प्रमुख तत्व, सूक्ष्ममात्रिक एवं दुर्लभ पृथ्वी तत्वों (REE) का भू–रसायनविज्ञान किया गया है। जिनसे दक्षिण विक्टोरिया भूमि, अंटार्कटिका की ऐलन पहाड़ियों में हिमयुगोत्तर दशाओं में कोयला संस्तरों से संघटित पादप स्थूल एवं सूक्ष्म जीवाश्मों के प्रचुर अभिलेख मिले हैं। भू–रसायनविज्ञान प्रबलता से वॉल्केनोजेनिक आगत के साथ फेल्सिक उद्गम–स्थल तथा अपक्षय व उष्णजलीय परिवर्तन की भूमिका सुझाता है। भू–रासायनिक विश्लेषण से व्युत्पन्न पुराजलवायवी विवेचन विलंबित पर्मियन के दौरान कोष्ण, शीतोष्ण व आर्द्र स्थितियां तथा विलंबित ट्राइएसिक के दौरान कोष्ण व आर्द्र स्थितियां इंगित करता है।

सूचक शब्द—भू–रसायनविज्ञान, पर्मियन, ट्राइएसिक, ऐलन पहाड़ियां, अंटार्कटिका।

INTRODUCTION

ANTARCTICA, presently one of the world's driest deserts and totally inhospitable to plant life, was a part of the Gondwana Supercontinent during Permian and Triassic along with other continents such as India, Australia, South America and South Africa. The melting of the late Carboniferous–Early Permian ice sheet led to amelioration of climate subsequently followed by a rapid evolution of the *Glossopteris* flora in the Gondwana continents. Extensive cold–temperate swamps with thriving plant communities of *Glossopteris* and other allied plants formed thick coal seams in different Gondwana basins. The trunks of the trees that bore *Glossopteris* leaves are marked by growth rings, reflecting the effects of strong seasonality. At the end of the Permian, when the climate became increasingly hot and dry with marked seasonality of rainfall, a new flora–the *Dicroidium* flora appeared in the Gondwana continents. The Permo–Triassic transition is an important time in the evolution of several groups of Gondwana plants, when *Dicroidium* flora gradually replaced the *Glossopteris* flora. Antarctica, too, fostered dense forests of *Glossopteris* and *Dicroidium* floras during Permian and Triassic, respectively.

The vegetation of Antarctica is of evolutionary significance since it encompasses not only early vascular land plants like bryophytes but also a number of higher plant orders such as Sphenophyllales, Filicales, Pteridospermales, Glossopteridales, Cordaitales Corystospermales, Cycadales and Pinales. A plethora of information is available on the Permian (Plumstead, 1975; Rigby, 1969; Rigby & Schopf, 1969; Schopf, 1968, 1976; Kräusel, 1962; Maheshwari, 1972; Chatterjee *et al.*, 1983; Gee, 1989; Pigg & Taylor, 1990, 1993; Smoot & Taylor, 1986; Taylor & Taylor, 1987; Taylor *et al.*, 1992; Retallack & Krull, 1999; Retallack *et al.*, 2005) and Triassic (Osborne & Taylor, 1989; Osborne *et al.,* 2000; Bose *et al.*, 1990 and references cited therein, Perovich & Taylor, 1989; Delevoryas *et al.*, 1992; Webb & Fielding, 1993; Taylor, 1996; Taylor *et al.,* 1994; Cantrill *et al.*, 1995; McLoughlin *et al.*, 1997; Yao *et al.*, 1995,1997; Phipps *et al.*, 1998; Axsmith *et al.*, 2000; Rothwell *et al.,* 2002; McManus *et al.,* 2002; Klavins *et al.,* 2002, 2003, 2004; Hermans *et al.,* 2007; Bomfleur & Kerp, 2010; Bomfleur *et al.*, 2007, 2011; Escapa *et al.*, 2011) megafloras of east and west, and central Transantarctic Mountains, Antarctica. Besides, several studies have been carried out on palynological (Balme & Playford, 1967; Kyle, 1977; Kyle & Schopf, 1982; Larson *et al.*, 1990; Farabee *et al.*, 1990; Lindstörm, 1996, 2005; Masood *et al.*, 1994; Askin, 1995; McLoughlin *et al.*, 1997; Ram–Awatar *et al.*, 2014), faunal (Hammer *et al.*, 2004; Retallack *et al.*, 2005 and references cited therein), palaeofire (Kumar *et al.*, 2011) geochemical and geophysical (Angino & Armitage*,* 1963; Weiss *et al.*, 1979; Saunders *et al.*, 1980; Kurat *et al.* 1994; Roex *et al.*, 1985; Zhao *et al.*, 1997; Khare *et al.*, 2009; Srivastava *et al.*, 2013), and petrological (Roex *et al.*, 1985; Kumar *et al.*, 2013) aspects.

The late Permian Weller Formation and the late Triassic Lashly Formation of Gondwana sequences in Allan Hills (latitude 76.72ºS, longitude 159.67ºE) of South Victoria Land, Antarctica have yielded rich record of plant mega–and micro fossils associated with coal beds in post–glacial conditions (Chatterjee *et al.*, 2013; Ram–Awatar *et al.*, 2014: Tewari *et al.*, 2015). The Weller Formation, which lies directly over the early Permian glacial strata, records a change from glacial to postglacial condition with the establishment of polar forest (Tewari *et al.*, 2015). Upward in the Gondwana sequence, thick coal beds occur in swamp and meandering stream facies of Weller and Lashly formations, while they are conspicuously absent in the intervening Feather Formation of channel deposits. Sedimentological (Retallack *et al.*, 2005) and petrographic (Kumar *et al.*, 2011) studies of these fossiliferous horizons exhibit microscopic charcoal remains, which suggest ancient forest fire events, possibly caused by continental volcanism (Kumar *et al.*, 2013). The preservation of carbonaceous material and the deposition of coal during Permian and Triassic were probably related to climatic changes, including increase in temperature and humidity.

Major, trace and rare earth element (REE) geochemistry has been found to be useful to characterize source–rock weathering and climatic variability from the terrestrial detritus of a basin (Nesbitt & Young, 1982; Cox *et al.*, 1995; Basu, 1976; Quasim et al., 2017). Their records are influenced by source rock lithologies, chemical weathering, sorting, sedimentation and post depositional diagenetic reactions (McLennan *et al.*, 1993). The distribution of these elements provides clues of the geological processes, provenance and tectonic setting (McLennan *et al.*, 1993; Cullers *et al.*, 1988; McLennan, 1989). The REE geochemistry has an added advantage over major and trace elements to decipher the provenance, since the concentration of these elements is not affected during erosion, sedimentation and diagenesis and thus represents a homogenized average source composition (McLennan, 1989; Bhatia, 1985; Nance & Taylor, 1976).

This paper attempts to investigate the geochemistry of two rock samples collected from the Permian Weller and Triassic Lashly formations to understand the source and composition of these rocks and their implication on palaeoclimate of the area.

GEOLOGICAL SETTING

The Beacon Supergroup crops out along the length of the Transantarctic Mountains and was deposited in a retroarc foreland basin (Collinson *et al.*, 2006). The exposures of this supergroup in the Allan Hills occur in the shape of a Y (Fig.

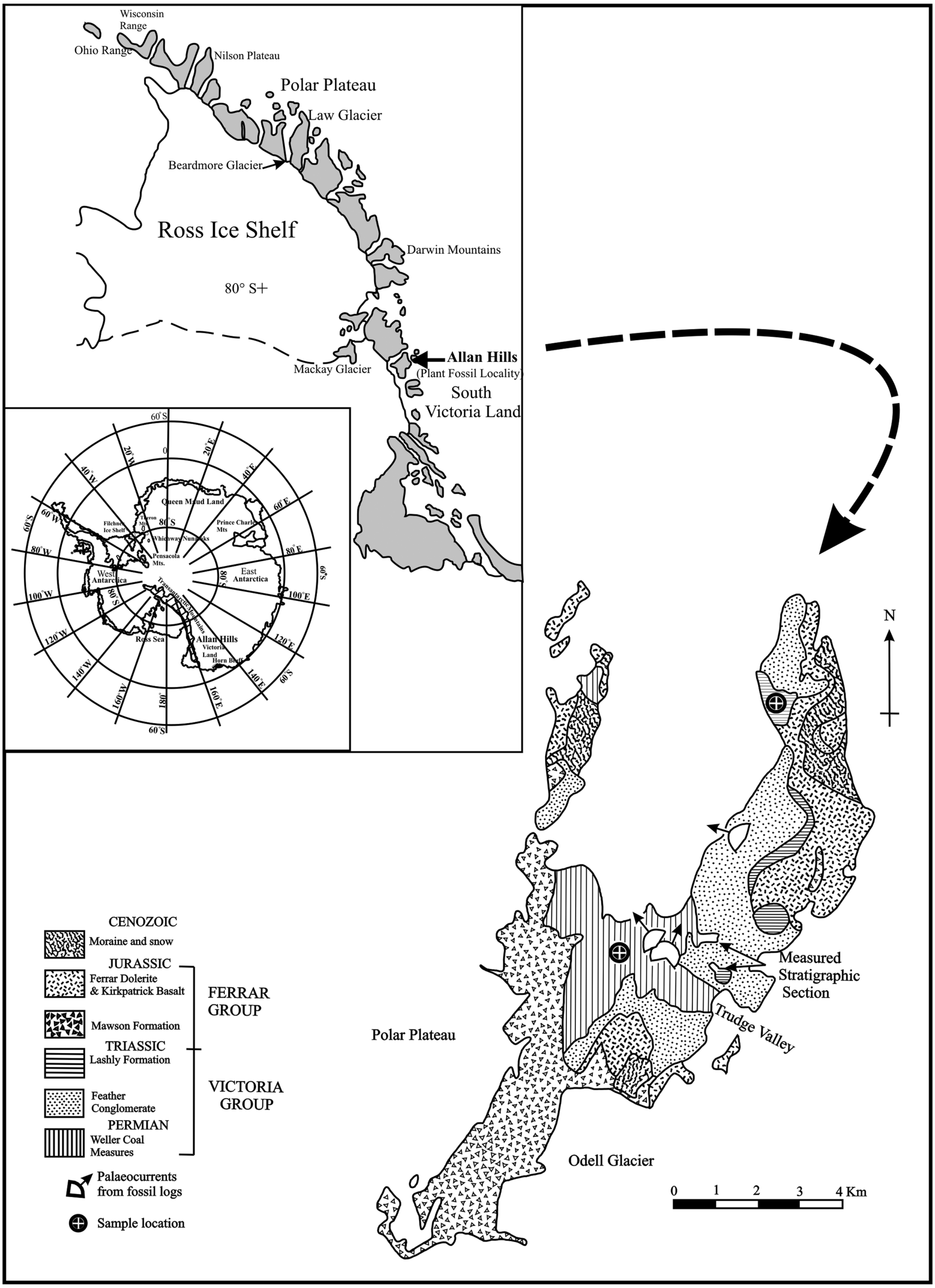

Fig. 1—Geological map of Allan Hills (marked by an arrow), South Victoria Land, central Transantarctic Mountains, Antarctica (modified after Kyle, 1977) showing the sample locations.

1) and are divided into two units: the lower Victoria Group of mainly fluvial siliciclastics, and the upper Ferrar Group of volcanic origin (Ballance, 1977; Chatterjee *et al*., 1983).

The stratigraphy of Allan Hills has been discussed by Gunn and Warren (1962), Borns and Hall (1969), Barrett *et al.* (1971), Barrett and Kohn (1975), Ballance (1977), Kyle (1977) and Collinson *et al*. (1987). The Permian–Triassic boundary is difficult to recognize in the non marine Gondwana sections of Antarctica. The Glossopteris flora in the Allan Hills is mainly restricted to Permian. Hence, most likely, the Permo−Triassic boundary in this region, if complete, would occur somewhere between the Weller Formation and the Feather Conglomerate. However, demarcation of the exact Permo−Triassic boundary in the Antarctic Gondwana sequences is highly controversial.

The Permo−Triassic Victoria Group consists of flat–lying continental sediments and ranges in age from Permian to Jurassic, and is exposed throughout much of the Transantartic Mountains. It consists of Permian glacial beds (the Metschel Tillite) at the base, which are overlain successively by the late Permian Weller Formation and the Triassic Feather and Lashly formations (Collinson *et al*., 2006). The Triassic strata are overlain disconformably by the Ferrar Group which comprises the lower Mawson Formation consisting mainly of diamictite and the upper Ferrar Formation which shows intrusions of sills and dykes of the Ferrar dolerite. The Mawson and Ferrar formations are of early and late Jurassic ages, respectively.

Chatterjee *et al*. (2013) have described the stratigraphic setup of the Weller and Lashley formations. The *Glossopteris*–bearing Weller Formation consists of conglomerate, arkosic sandstone, shale, and coal in fining–upwards cycle. The Formation is about 250 meters thick and is easily recognizable from its coal–bearing horizons. It consists of three members: A, B, and C.

The Triassic Lashly Formation, which is more than 500 m thick, is a succession of cyclic medium–to fine grained sandstone and carbonaceous plant–bearing mudstone and siltstone beds. It gradationally overlies the Feather Conglomerate. Barrett and Kohn (1975) subdivided the Lashly Formation into four informal members (A through D), where the lower part (members A and B) is more volcaniclastic than the quartzose upper part of the formation (members C and D; Collinson *et al.*, 1987; Fig. 2).

METHODOLOGY

For geochemical analysis, representative samples from coal bearing strata of carbonaceous shale (from Member C of the Permian Weller Formation) and green shale (from Member C of the Triassic Lashly Formation) were selected and ground to 80 mesh standard sieve size. One portion of the screened samples was ground to about 200 mesh using agate mortar and pestle. Pressed powder pellets were prepared by mixing with 4–5 drops of polyvinyl alcohol as binding agent (Stork *et al.*, 1987; Saini *et al*., 2002). The pellets were analyzed for the major and trace elemental abundance by standard Wavelength Dispersive X–ray Flourescence Spectrometer (Siemens SRS–3000) at Wadia Institute of Himalayan Geology, Dehradun (WIHG). REEs (rare earth elements) were determined using ICP–MS (PerkinElmer, Elan–DRCe) at WIHG, Dehradun using the methodology as reported by Khanna *et al.* (2009). The analytical results were consistent with the International Geostandard Reference values with mean percent deviation 2−5% for major oxides, 12% for trace elements and 1−15% for REE and are displayed as Table 1. The chondrite–normalized REE plot is shown in Fig. 3.

RESULTS AND DISCUSSION

The major and trace element contents particularly high zirconium concentration (100 to 165 ppm), high La/Yb_N = 4.07 to 9.73 ratios, negative Eu anomalies along with the tetrad effect in both the shale samples suggest dominantly of a felsic provenance/source and with a volcanogenic input during their deposition. The high loss on ignition (7.4–12.6 wt %) indicate that the samples have undergone high degree of weathering/alteration to become soils/palaeosols.

Concentration of ΣREE in the two samples ranges from 107.56 to 193.8 ppm. The chondrite–normalized REE composition of the samples in general exhibit similar patterns with overlapping abundances of heavy REE. The patterns are characterized by LREE (Light Rare Earth elements) enrichment (La_N/Sm_N = 2.41–3.8), relatively flat HREE (Heavy Rare Earth elements) (Gd_N/ Yb_N = 1.25–1.69) but with a prominent tetrad effect and negative Eu anomalies (Eu/Eu* = 0.54–0.88). High abundances of light REE in the carbonaceous shale relative to green shale is due to its higher contents of Fe_2O_3 (20.4 wt %) and MnO (2.63 wt %) with which they could have co–precipitated during weathering, and redistribution during hydrothermal alteration.

Interestingly, both the samples exhibit clearly the third tetrad (T_3: Gd–Tb–Dy–Ho, i.e. M−type) and fourth tetrad (T_4: Er–Tm–Yb–Lu, i.e. W−type) effect (Fig. 3). The coexistence of composite M− and W−type of REE tetrad effect in the same samples indicates the involvement of aqueous fluids during weathering and hydrothermal processes. It has been found experimentally that aqueous fluids contribute to the formation of M− and W−type of REE tetrad effect. Similar kind of tetrad effect were also reported in H_2O/aqueous bearing phases such as soils, pegmatites, tuffaceous rock with clastic minerals and lignite (Feng, 2010). This is because the different electronic configuration of REE affects their complexing behaviour in weathering system. Therefore, the variable stability of REE complexes, in general and heavy REE in particular in aqueous solution causes the REE fractionation and tetrad effect occurrence during their mobilization and redistribution in the

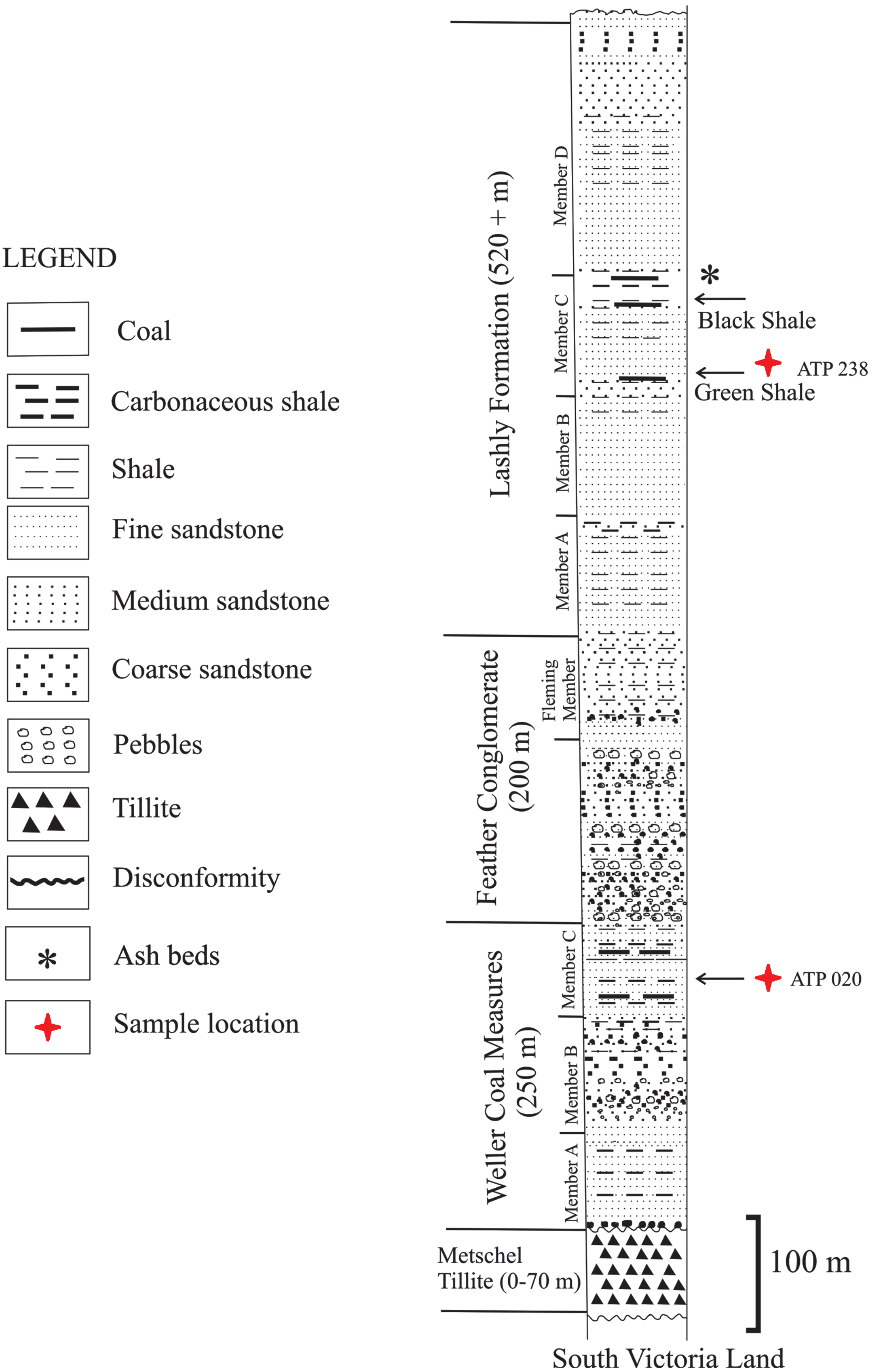

Fig. 2—Litholog of the Victoria Group in South Victoria Land (after Kyle, 1977) showing sample locations.

Table 1—Major, Trace and REE analysis of Permian carbonaceous shale (ATP 020) and Triassic green shale (ATP 238).

ITEM	Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	SUM	LOI
Major Oxides	ATP020	0.92	0.89	15.64	69.64	0.01	3.4	0.18	0.62	0.02	2.63	93.95	7.41
	ATP238	1.19	1.34	10.08	51.64	0.21	0.78	2.05	0.45	0.53	20.4	88.67	12.66

all values in %

		Ba	Cr	V	Sc	Co	Ni	Cu	Zn	Ga	Pb	Th	Rb	U	Sr	Y	Zr	Nb
Trace Elements	ATP020	901	64	83	12	51	20	31	63	22	16	26	182	2.6	96	27	165	15
	ATP238	116	32	92	9	30	42	30	65	20	24	5	40	2.98	180	28	100	5

all values in PPM

		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
REE	ATP020	19	39	4.5	20.8	4.78	1.22	4.78	0.84	4.76	0.99	2.86	0.46	3.07	0.5
	ATP238	43.7	66.2	8.9	45.9	6.99	1.32	6.26	1.02	5.5	1.09	3.07	0.47	2.96	0.43

weathered profile/palaeosoils (Masuda *et al.*, 1987; Siddaiah *et al.*, 1994; Feng, 2010). Although, the tetrad effect was studied in igneous/magmatic systems and marine sediments, but very little is known about its development during REE mobilization, transfer, precipitation, and redistribution under weathering conditions (Feng, 2010).

The deviation from the normal linear trend of chondrite–normalized REE patterns, the striking and characteristic REE tetrad effect observed in the carbonaceous shale and green shale must be an indication of peculiar geochemical processes involved. The prominent M–and W–type tetrad effect and high Y/Ho ratio (26 to 27) in the samples studied indicates that remarkable fractionation between Y and Ho occurred during weathering process. All the geochemical characters of both the sediment samples indicate the role of weathering and hydrothermal alteration in their genesis/formation, and belong to incipient to moderately developed palaeosols. The carbonaceous shale (sample ATP020) from Permian Weller Formation has undergone intense weathering and extensive ferruginization than the Triassic green shale (sample ATP238) indicating a warmer and wetter climate.

The proliferation of *Glossopteris* flora during the late Permian also suggests warm, temperate and humid climatic conditions, which were suitable for the formation of coal. However, during the early Triassic, the climate became increasingly hot and dry with marked seasonality of rainfall. As a consequence, coal is absent and development of red–beds is manifested in almost all the Gondwana basins (Rettalack, *et al.*, 1996; McLoughlin *et al.* 1997; McLoughlin, 2001). The advent of Triassic is marked by the evolution of a new flora–the *Dicroidium* flora (Lele, 1976). By the late Triassic, when the climatic conditions became warm and humid, several gymnospermous plant orders comprising Bennettitales, Pentoxylales, Peltaspermales, Cycadales, Pinales, Ginkgoales and Gnetales flourished in many Gondwanan countries (Townrow, 1966; Archangelsky, 1968; Holmes & Ash, 1979; Pal, 1984; Anderson & Anderson, 1983, 1985, 1989; Bose *et al.*, 1990; Pattemore & Rigby, 2001; Bomfleur & Kerp, 2010; Moison *et al.*, 2010).

The palaeoclimatic interpretation derived from geochemical analysis of the Antarctic samples, in general, corroborates with the earlier interpretations of the climate based on plant fossils and formation of coal which indicate warm, temperate and humid conditions during the late Permian, and warm and humid conditions reflected by presence of dicynodont vertebrates and thick *Dicroidium* forests during the late Triassic. However, warmer climate of Weller Formation as compared to that of the Lashly Formation of Allan hills may be a local variation.

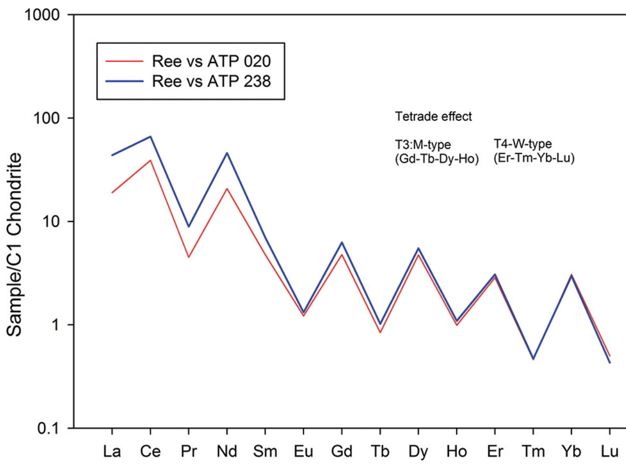

Fig. 3—Chondrite–normalized REE patterns for Carbonaceous shale (ATP 020) and Green shale (ATP238) showing composite T_3 & T_4 tetrad effect.

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