

Appendix I

Methodology

Analytical Techniques



1. Introduction

The appendix provides further information related to the provenance study of the Neoproterozoic Ventersdorp Supergroup and its age related supracrustal rocks of the Kaapvaal Craton, South Africa. It comprises the required detail of the analytical techniques used in this study (Appendix I). Furthermore, the different formations are presented in detail with a description of their petrographic and geochemical characteristics (Appendix II). Zircon geochronological data and stable isotope data, and drill core logs are compiled in Appendix III, IV and V, respectively.

2. Analytical Techniques

2.1. Petrography

The analysis of the framework mineralogy of sedimentary rocks yields a first impression of their mineralogical composition and the depositional environment. Point-counting methods after Gazzi-Dickinson are the most useful tool to understand the framework mineralogy and to identify alteration and other weathering and diagenetic effects (Dickinson and Suczek, 1979; Ingersoll et al., 1984). However, point-counting after Gazzi-Dickinson is only suitable for sedimentary rocks with grain sizes $\geq 63 \mu\text{m}$ and less than 15% matrix (Dickinson, 1970). The sedimentary rocks studied in this thesis consist of matrix-rich wacke and quartz-rich arenites that display variable grain sizes, so that none of the samples is ideally suitable for this point-counting method. Hence, instead of actual point counting, the volume percentages for framework minerals observed in thin sections were estimated after detailed study. The mineralogical composition of lithologies that are too fine-grained for transmitted light microscopy was studied using scanning electron microscopy and X-ray powder diffractometry.

Another important tool for provenance studies is the identification of heavy mineral associations (Mange and Maurer, 1995; Morton and Hurst, 1995). Populations of heavy minerals can be quantified to recognize changes in the lithostratigraphic column of the investigated formation (Boenick, 1983). SEM-EDS or EMP analyses of the mineral chemistry of specific heavy minerals like magnetite, chromite, rutile and garnet provide further insight in the source of the deposits (Basu and Molinaroli,

1991; Morton et al., 1992; Krawinkel et al., 1999, von Eynatten and Gaupp, 1999). In this study, only SEM-EDS were performed to identify the mineralogical composition of the heavy mineral associations qualitatively. Analyses of single rutile and chromite grains using the microprobe turned out to be unsuccessful, since standards necessary to determine the concentrations of the provenance indicating elements including Ti, Sn, W, Nb, Al and Cr in rutile, were not available.

2.2. Whole Rock Geochemistry

2.2.1. Major elements

The concentrations of major elements can be affected by diagenesis and metamorphism, so that prior to any interpretation their mobility must be studied (McLennan, 2001).

The calculation of the chemical index of chemical alteration (CIA; Nesbitt and Young, 1982) is a useful means to describe the degree of weathering. Its calculation uses molecular concentrations: $CIA = [Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O)] * 100$. CaO^* is the calcite bound in silicates. Unweathered granite has a CIA of 50, whereas average shale ranges around values of 75 (Fedo et al., 1995). The closer the CIA to a value of 100, the more weathered is the rock. It reflects the alteration of volcanic glass and feldspar to clay minerals. Furthermore, deviations from ideal weathering trends can give information on the type of alteration, as for example K-metasomatism, which discloses the alteration of plagioclase to K-feldspar and from Al-rich clay minerals to illite (Fedo et al., 1995).

Ideally, a rock needs to contain less than 75 wt.% SiO_2 and less than 1 wt.% CaO to calculate a reliable CIA. However, most sedimentary rocks analysed in this study have much higher SiO_2 -concentrations, and are often rich in carbonate-bound CaO . The calculation of CaO^* led to negative values, so that it was assumed that all CaO is related to the presence of carbonate minerals. Thus, the CIA values need to be interpreted with caution.

The plagioclase index of alteration (PIA) was determined following Fedo et al. (1995). For this index, K_2O molecular concentrations are excluded from the CIA formula: $PIA = [(Al_2O_3 - K_2O) / (Al_2O_3 + CaO^* + Na_2O - K_2O)] * 100$. Thus, the PIA generally reports higher values than the CIA, in particular for K-metasomatized rocks.

In this study, the PIA turned out to be valuable, as most of the rocks are affected by K-metasomatism, which lowers the CIA. The combination of PIA and CIA avoids misleading interpretation of too low CIA values and reveals a more realistic degree of chemical weathering.

A further means to establish the degree of chemical alteration is the K/Cs ratio (McLennan et al., 1990). Cs is enriched in clay minerals during weathering, which leads to a decrease in K/Cs ratios of the rocks with increasing weathering. However, K-metasomatism, as established through CIA and PIA values, resets the K/Cs ratio, so that it becomes difficult to interpret for the quantification of chemical weathering.

The Th/U ratio is often used in relation to Th- and U-concentrations to present weathering under oxidizing conditions (McLennan et al., 1993; Hurowitz and McLennan, 2005). Weathering under oxidizing conditions results in the mobilization of U as U^{6+} , whereas Th remains immobile causing Th/U ratios to increase significantly. However, it is widely accepted that up to ca. 2.45 Ga, the atmosphere was very low in oxygen (e.g. Bekker et al., 2004; Hannah et al., 2004; Barley et al., 2005), so that this means of presentation of weathering as a result of reworking may not be suitable for the Neoproterozoic rocks analysed in this study. Nevertheless, diagrams of Th/U versus U and Th/U versus Th are presented.

2.2.2. Trace and Rare Earth Elements (REE)

Immobile trace element and REE compositions are resistant to diagenesis and metamorphism (McLennan et al., 1993), whereas diagenesis and metamorphism affect mobile trace elements (McLennan, 2001). Thus, analyses of immobile trace elements and REE present a reliable means of information for provenance studies. Especially the REE are useful provenance indicators (McLennan et al., 1990; Bock et al., 2000; McLennan, 2001), because they are immobile under surface conditions and possess short residence times in seawater, so that they represent the characteristics of the parental rock composition in the sedimentary rock record (Taylor and McLennan, 1985; McLennan, 1989). Valuable parameters that describe REE-patterns, which are important for the characterisation of the source rocks, are for example La_N/Yb_N ratios or the Eu-anomaly.

Another useful discrimination diagram to describe source rock compositions are the Zr/Ti – Nb/Y discrimination diagram after Winchester and Floyd (1977), and the

Th/Sc – Zr/Sc diagram after McLennan et al. (1993). The former is normally used to discriminate between volcanic rocks, but it can also be used to describe the degree of fractionation of the source rocks that contributed to the deposition of the studied sedimentary rocks (e.g. Fralick, 2003; van Staden, 2006). The Th/Sc – Zr/Sc plot gives insight in the degree of fractionation of the source rocks, which is expressed in the Th/Sc ratio, where Th is incompatible and Sc compatible in magmatic processes. Furthermore, this plot describes the degree of sediment recycling that is expressed in the Zr/Sc ratio. Increased recycling concentrates zircon in sedimentary rocks (increase in Zr-concentrations) on the expense of volcanic material contained in the detritus (decrease in Sc-concentrations).

Finally, trace elements such as La, Th, Zr, Nb, Y, Sc, Co and Ti have been recognized as valuable provenance indicators for shales, arenites and wackes (Taylor and McLennan, 1985; Bhatia and Crook, 1986; McLennan et al., 1990). Bivariate plots of Ti/Zr – La/Sc, as well as triangular La-Th-Sc and Th-Sc-Zr/10 plots are useful means to discriminate the tectonic settings of clastic sedimentary rocks (Bhatia and Crook, 1986). However, in this study these diagrams need to be tested for their suitability on Neoarchaean rocks, as they are only applicable if the plate-tectonic processes that formed these supracrustal rocks are the same as the modern ones that are active today.

2.2.3. Isotope Geochemistry

The Nd-isotopic systematics is believed to be resistant to alteration processes (McLennan et al., 1993). They remain unchanged even during high-grade metamorphism, so that they present an important method to study the provenance of sedimentary rocks that have suffered an intermediate- to high-grade metamorphic overprint (Lucassen et al., 2000). Hence, contributions of detritus from different terranes with differing crustal compositions and evolution can be identified using Nd isotopic systematics (De Paolo and Wasserburg, 1976; McCulloch and Wasserburg, 1978; De LaPaolo, 1981, 1988). While the Nd-model ages give the average crustal residence age, $\epsilon_{Nd}(t)$ and $f_{Sm/Nd}$ are meaningful parameters to characterize and compare the analysed rocks. The $f_{Sm/Nd} - \epsilon_{Nd}(t)$ diagram gives evidence on the Sm/Nd ratio in combination with the Nd-isotopic data at the time of deposition (Bock et al., 1994). $f_{Sm/Nd} = 0$ reflects a chondritic composition, while negative values are explained by crustal contamination (Taylor and McLennan, 1985).

Rb-Sr isotopic systematics is also an important means for geochronological studies, since many rock-forming minerals contain Rb and Sr (Faure, 2001). However, complex histories of sedimentary rocks, including mixing of source rocks, changes in Rb- and Sr-concentrations, and re-equilibration of the Rb-Sr isotopic systematics make the interpretation of Rb-Sr isotopic data difficult (Faure, 2001). Rb-Sr isotopic systematics in this study were used to investigate a probable disturbance of the Neoproterozoic supracrustal successions and the implications of such event for the evolution of the Kaapvaal Craton.

2.3. Suitability of provenance indicators for Archaean rocks

Provenance indicating diagrams were generated using Palaeozoic to recent sandstones and shales (e.g. Taylor and McLennan, 1985; Bhatia and Crook, 1986; Floyd and Leveridge, 1987; McLennan et al., 1990, 1993). However, Archaean upper continental crust evolved under different magmatic and tectonic processes (Chapter 1), which leaves the provenance analysis of Archaean rocks problematic. Thus, the diagrams regarding the defined fields may not be suitable for the identification of a tectonic setting related to Archaean tectonic processes. Therefore, the emphasis is put on trends rather than on determining a palaeotectonic setting according to the defined fields.

Geochemical results were compared to both Archaean and post-Archaean upper continental crust to reveal similarities and differences, especially with regards to rare earth element and other trace element concentrations that vary noticeably between Archaean and post-Archaean upper continental crust composition (Taylor and McLennan, 1985; McLennan et al., 2006). The motivation to use geochemical signatures is to highlight differences or trends, as well as signatures that are unusual for post-Archaean upper continental crust.

2.4. References

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3. Lower Limits of Detection

Table I.1 Lower limits of detection (lld) for geochemical analyses using XRF at SPECTRAU. All data are reported in ppm.

application	Basalt	Basalt	Intermediate	Intermediate	Granitic	Granitic
	Bead 2	PPow 2	Bead 2	PPow 2	Bead 3	PPow 2
SiO ₂	56.79	12.17	48.46	-	-	111.52
Al ₂ O ₃	-	66.75	-	40.68	45.64	-
MgO	19.49	19.76	37.44	11.3	14.86	2.59
TiO ₂	7.42	-	7.97	2.22	8.17	1.69
Fe ₂ O ₃	5.46	9.31	5.46	2.51	43.15	-
CaO	-	-	8.23	3.53	9.72	-
Na ₂ O	35.24	-	28.62	11.94	22.31	2.89
K ₂ O	6.5	-	6.64	-	13.17	-
MnO	4.13	2.57	3.7	-	6.35	1.62
P ₂ O ₅	5.04	0	3.25	-	4.5	0.9
Ba				4.05		5.45
Nb		0.31		0.29		0.24
Pb				0.62		0.52
Rb		0.32		0.23		0.23
Sr		0.42		0.28		0.26
Th				0.74		0.87
Y		0.2		0.23		0.34
Zr		0.21		0.18		0.2
Ce				1.27		1.61
Co		0.38		1		0.99
Cr		1.4		1.41		1.08
Cu		0.57		1.16		0.89
Ga				0.41		0.37
Hf				0.3		0.57
La				4.47		6.01
S				0.21		0.38
Zn		0.69		0.62		0.41
Ni		1.18		1.02		0
V		0.68		1.48		0.75

-: not calculated. 0: lld below 0. Blank fields: element not analysed using the specific application.

4. Accuracy of XRF measurements

To control the accuracy of the measurements of major and selected trace elements, standards were added to the sample batches. The standard closest to the composition of the wackes and arenites is JR-1. However, its SiO₂-concentration is with 75 wt.% still lower than that of most of the analysed samples. Other standards available, such as AC-E, AN-G and GS-N, were not considered for the calculation of the accuracy, because their SiO₂-concentrations were with 65 wt.% much lower. Table I.2 presents the average of JR-1 measurements in comparison with the certified reference values.

Table I.2 Measured major and trace element concentrations for standard JR-1 in comparison to its reference concentrations. Major element concentrations are reported in wt.%, trace element concentrations are reported in ppm.

	JR-1 ^a	certified reference value	accuracy
SiO ₂	74.0	75.5	98.13%
Al ₂ O ₃	12.5	12.8	97.81%
TiO ₂	0.09	0.11	83.64%
MgO	0.12	0.12	100.42%
CaO	0.66	0.67	98.96%
Na ₂ O	4.10	4.02	101.97%
K ₂ O	4.39	4.41	99.61%
P ₂ O ₅	0.02	0.02	76.19%
Fe ₂ O ₃	0.67	0.89	75.34%
MnO	0.09	0.10	90.91%
Nb	14	15	88.82%
Rb	286	257	111.44%
Sr	30	29	102.06%
Y	44	45	98.23%
Zr	91	100	91.09%
Cu	3	3	97.01%
Zn	31	31	101.96%
V	6	7	90.00%

^a: average of two (major elements) and three (trace elements) analyses.