



Department of
Industry and Resources

**RECORD
2007/14**

**COMPOSITION OF THE BUNBURY BASALT
(BB1) AND KERBA MONZOGRAHITE (KG1)
GEOCHEMICAL REFERENCE MATERIALS,
AND ASSESSING THE CONTAMINATION
EFFECTS OF MILL HEADS**

by PA Morris



Geological Survey of Western Australia



GEOLOGICAL SURVEY OF WESTERN AUSTRALIA

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Perth 2007

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REFERENCE

The recommended reference for this publication is:

Morris, PA, 2007, Composition of the Bunbury basalt (BB1) and Kerba Monzogranite (KG1) geochemical reference materials, and assessing the contamination effects of mill heads: Geological Survey of Western Australia, Record 2007/14, 22p.

National Library of Australia Card Number and ISBN 978-174168-130-7 (PDF)

Grid references in this publication refer to the Geocentric Datum of Australia 1994 (GDA94). Locations mentioned in the text are referenced using Map Grid Australia (MGA) coordinates, Zone 50. All locations are quoted to at least the nearest 100 m.

Cover image modified from Landsat data, courtesy of ACRES

Published 2007 by Geological Survey of Western Australia

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Composition of the Bunbury Basalt (BB1) and Kerba Monzogranite (KG1) geochemical reference materials, and assessing the contamination effects of mill heads

by

PA Morris

Abstract

A series of working and suggested values are presented for two geochemical reference materials — Bunbury Basalt (BB1) and Kerba Monzogranite (KG1) — derived from data generated at several commercial laboratories, and a government and a university laboratory.

For analytes where there are more than five analyses, and the analyte concentration is above the lower level of detection, data have been statistically treated in a sequential fashion. Firstly, outliers have been removed by excluding values that lie beyond one standard deviation of the mean. The resulting trimmed data have been averaged, with this value taken as a working value, and the limits of acceptability set as values that fall within two standard deviations of the mean. Where there are less than five analyses, or most data are less than the lower level of detection, suggested values have been tabulated.

The analysis of Ba, Rb, Sr, Y, Pb, and Zr by both X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) at Geoscience Australia's Canberra laboratory means that data can be assessed according to technique. For some elements (e.g. Zr) there is a wider spread in ICP-MS data compared to that determined by XRF, which is attributed to incomplete sample dissolution prior to ICP analysis. A systematic difference in the mean values for Ba and Rb is evident according to technique. Future work requires the better characterization of several elements found at low concentrations in both reference materials, including Hg, Tl, Te, Bi, Ag, Pd, Pt, Re, and Rh.

Analysis of Bunbury Basalt milled in three separate mill heads (tungsten carbide, low-chrome steel, and zirconia) shows that significant contamination of W and Co is introduced from the tungsten-carbide mill head, with Cr and Ni introduced from the low-chrome steel mill head. Apart from Zr the zirconia mill head introduces rare earth elements and elements such as Ba, Sr, Th, Y, and Zn, due to its composition and lower durability. Testing shows that petrogenetically important elements such as Hf, Ta, and Nb (commonly found at low concentrations in mafic rocks) have not been noticeably affected by milling in either tungsten-carbide or low-chrome steel mill heads.

KEYWORDS: reference material, geochemistry, analysis, contamination.

Introduction

Regular monitoring of data quality during geochemical analysis is an important part of analytical programs. Typically, this is achieved by analysis of more than one aliquot of the same sample (duplicate) and analysis of a material whose composition is well known through previous cycles of analysis at different laboratories under well-constrained conditions (a standard or certified reference material (CRM; Kane, 1992). Although duplicate analyses can be used to gauge analytical precision (i.e. the degree of agreement between analyses obtained under set conditions; Thompson and Ramsey, 1995), repeat analyses of certified reference materials can be used to gauge not only precision,

but also accuracy (i.e. how close a measurement is to the true value; Thompson and Ramsey, 1995). The GeoREM database at <<http://georem.mpch-mainz.gwdg.de>> contains a variety of data for reference materials related to geological and environmental science.

Although most laboratories routinely include materials of a known composition during analytical runs in order to monitor data quality, several factors may limit the usefulness of these reference materials. In some cases analyte concentrations of reference materials may be several orders of magnitude different to those of unknown samples. In other cases the matrix of the reference material may be different to that of unknowns (e.g. oxides versus

silicates), and in particular cases, there is a limited amount of reliable data for certain analytes for particular digests or analytical techniques.

The importance of maintaining quality assurance and quality control (i.e. QAQC) by the analysis of well-characterized reference materials has been documented in several published studies. Hall and Plant (1992) evaluated the performance of commercial laboratories in determining trace element concentrations for use in tectonic setting discrimination. They found that some preparation techniques (e.g. mixed acid digestion) resulted in incomplete sample dissolution leading to spurious rare earth element (REE) concentrations, and poor accuracy for elements including Zr, Nb, Hf, and Ta. This resulted in assigning some samples to the wrong tectonic setting. Their study also showed that because several key trace elements were found at low concentrations, confidence in the accuracy and precision of these elements at close to the level of detection required the contemporaneous analysis of well-characterized reference materials. A related issue when dealing with elements at low concentrations is the common practice of presenting analytical data as multi-element normalized diagrams (spider plots), where normalization values are low and cited to a high level of precision (e.g. typically, mid-ocean ridge basalts (MORB) have low normalizing factors of Cs (0.007 ppm), Nb (2.33 ppm), Ta (0.132 ppm), La (2.5 ppm), and Yb (3.05 ppm); Sun and McDonough, 1989). For such diagrams to be meaningful, analytical precision and accuracy should be of equal magnitude to the normalization factors under consideration.

In a discussion of advances made in geochemical analysis, Hall (1996) noted that despite increasing sophistication of analytical techniques, routine analysis by commercial laboratories still produced erroneous results. She cited gold data generated during a certification exercise carried out by Canadian commercial laboratories for a variety of reference materials. The range for one standard was 1.3 to 2588 ppb Au, with a recommended value of 2.9 ppb Au. Although some of this variability could be attributed to sample inhomogeneity, a variation of three orders of magnitude indicates some laboratory-related issue, probably involving inaccurate calibration, contamination or poor sample handling. This study shows that inclusion of CRMs in analytical programs is essential to identify such problems.

Although well-characterized certified reference materials (Govindaraju, 1989; Ando et al., 1990; Potts et al., 1992; Gladney and Goode, 1981) are available commercially, they are commonly only supplied in small quantities for individual or institution use, which precludes their usefulness when routine analytical procedures can use up to 50 g for a single analysis (e.g. gold analysis by fire assay; Hoffman et al., 1998). This has resulted in commercial laboratories and mineral exploration companies in particular generating their own (inhouse) CRMs. This approach not only enables the preparation of sufficient material, but also means that CRMs can be individually tailored in terms of matrix type and analyte concentrations. Morris (2000) reported on the composition of 11 inhouse reference materials available within the Geological Survey of Western Australia (GSWA). While these were sufficiently well

characterized to be of use in analytical programs, many of them have nonsilicate matrices (e.g. copper ore, telluride ore, laterite, gossan) and most are mineralized, meaning that they have relatively high concentrations of some elements relative to normal crustal abundances. The need for unmineralized silicate-matrix reference materials has been emphasized by the increased amount of lithochemical analysis being undertaken by GSWA in conjunction with Geoscience Australia as part of the National Geoscience Accord. Under this agreement GSWA is generating about 500 whole-rock major element oxide, trace element, and REE (La–Lu) analyses at Geoscience Australia's Canberra laboratory per year, using a combination of X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometric (ICP-MS) analysis (Pyke, 2000; Eggins et al., 1997). In addition, an increasing number of these samples are also being analysed for Au, Pd, and Pt by commercial laboratories, some of whom are now offering sub-ppb detection levels (e.g. Richardson and Burnham, 2003).

Since most rocks analysed by GSWA are unmineralized silicate rocks, two new GSWA reference materials have been prepared, comprising a basalt (BB1) from near Bunbury and a monzogranite (KG1) from the western part of the Capricorn Orogen (Fig. 1). The composition of these two reference materials effectively brackets the compositional range of most silicate rocks analysed by GSWA. In this Record analyses of both reference materials from several laboratories are assessed, and a series of

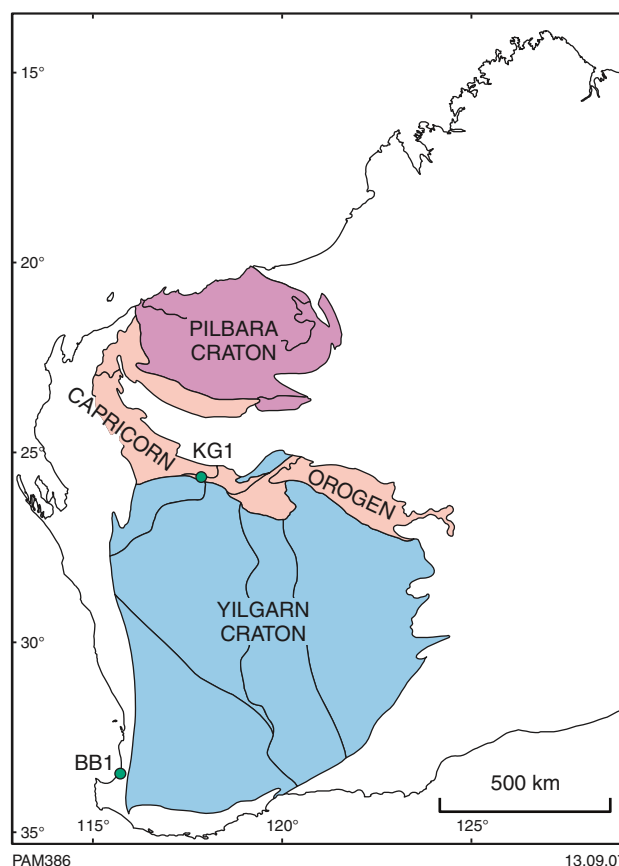


Figure 1. Location of the Bunbury Basalt (BB1) and Kerba Monzogranite (KG1) reference materials shown in relation to the simplified geology of Western Australia

working and suggested values are tabulated that can be used for quality assurance and quality control purposes.

Chemical reference material preparation

About 200 kg of BB1 (as crushed fragments with a maximum size of 10 cm diameter) and 100 kg of KG1 (as fresh blocks up to 20 cm diameter) were prepared at Gannet Holdings, Naval Base, Perth. Initial size reduction of each sample to 6 mm nominal diameter was carried out using a Jacques jaw crusher fitted with manganese-hardened steel plates. Milling of BB1 was carried out in a vibratory steel ball and rod mill under closed-circuit conditions, with all material air classified; this system recycles any coarse material back to the mill until all material attains a <75 µm particle size. Due to the smaller overall volume of material prepared, the Kerba Monzogranite was milled in steel LM5 ring mills and air classified as above to a nominal particle size of <75 µm.

Each resulting pulp was thoroughly mixed in a V blender, and packed into individual 1 kg foil-lined bags, thus ensuring that the pulp does not degenerate due to exposure to moisture or temperature over time.

Data evaluation

Geochemical analysis carried out by a variety of laboratories using different preparation and analytical techniques can result in a range in element concentrations for a single analyte in one material. In most cases differences in element concentrations can be attributed to different analytical approaches (e.g. aqua regia digest compared to 4-acid digest), but in some cases disparate results also reflect bad laboratory practice.

Procedures for either rejecting or accepting data that are used to chemically characterize reference materials are not well constrained. In a survey of available data from the literature for eight reference materials, Gladney and Goode (1981) excluded high and low values on subjective grounds. Following this, they calculated the mean $\pm 2 \times$ standard deviation (i.e. 2SD) of the trimmed dataset. They did not calculate these data for elements for which there were less than three available reports,

and where there were few data only concentration ranges were reported. They argued that the mean values for individual analytes should not be taken as 'recommended', 'certified', or 'best', but should be taken as 'usable'. In order to minimize bias in assessing analytical data, Potts et al. (1992) suggested that various approaches could be adopted, including only considering data generated by laboratories with a proven track record or using the approach of Gladney and Goode (1981).

A related issue is the reliability of data at concentrations close to the tolerance of the analytical technique. As discussed by Thompson (1992) and Thompson and Ramsey (1995), precision decreases as the concentration of the analyte approaches the lower level of detection (commonly called the 'detection level' or LLD), which can be taken as the analyte concentration equal to the blank level plus three times the standard deviation of the blank reading (IUPAC, 1978); alternatively, Hellman (1999) argued that a more realistic LLD is a level between 20 and 50 times the quoted LLD, above which precision is stable. In GSWA's regolith geochemistry program, statistical analysis is not carried out on sample populations where analyte levels are less than ten times the detection level (Morris and Verren, 2000).

In this Record data are screened in a stepwise fashion. For each analyte, if there are five or more analyses and the analyte concentration is above the lower level of detection, the data have been statistically treated. Analyses have been excluded if they lie beyond the mean ± 1 SD for the whole dataset. Following this the mean value of the remaining data is calculated and designated as the **working value**. The **acceptable range** of these trimmed data is taken as the mean ± 2 SD. Where there are fewer than five analyses and/or data are less than the detection level, **suggested values** have been tabulated. These suggested values are indicative of likely concentrations based on the available data and have not been quantitatively generated.

The complete dataset for both reference materials are presented in digital form as Appendices 1 and 2. A negative value indicates that the analyte concentration is below the detection level cited by the laboratory, and blanks indicate that the analyte has not been determined. To preserve anonymity codes are used for laboratories apart from Geoscience Australia. Acronyms for analytical preparation and finish are summarized in Table 1.

Table 1. Explanation of generic acronyms for analytical preparation and finishes used by participating laboratories

<i>Acronym</i>	<i>Explanation</i>
XRF	X-ray fluorescence
ICP	Inductively coupled plasma
Fusion/ICP	Alkaline oxidative fusion and ICP finish
4-acid ICP	4-acid digest and ICP finish
FA	Fire assay analysis
LECO	Analysis by LECO furnace
CVAP	Cold Vapour Generation Atomic Absorption Spectrometry
AR-ICP	Aqua regia digest and ICP finish
ME-MS42	Fire assay preconcentration and ICP-mass spectrometric finish
Fusion/ICP-OES	Alkaline oxidative fusion and ICP-optical emission spectrometric finish
4-acid ICP-MS	4-acid digest and ICP-mass spectrometric finish

Bunbury Basalt (BB1)

The Bunbury Basalt is found in two main areas of southwest Western Australia: near Bunbury (Fig. 1), and about 120 km to the south at Black Point (Frey et al., 1996). It is composed of a series of subaerial flow units, with individual flows up to 48 m thick. Based on distribution, radiometric dating, petrography, and geochemistry, Frey et al. (1996) divided the Bunbury Basalt into the c. 130 Ma Casuarina type (Bunbury), and the c. 123 Ma Gosselin type (Black Point). Frey et al. (1996) described the Bunbury Basalt as fine grained and vesicular, with the Casuarina type being more coarsely porphyritic than the Gosselin type. Phenocrysts comprise plagioclase and pyroxene with or without opaque oxide. The matrix contains glass and is commonly altered to some extent. Reference material BB1 is part of the Casuarina type, from a quarry at Gelorup, about 7 km south of Bunbury (Zone 50, MGA 375756E 6302681N; Fig. 2).

A total of 52 major element oxide and loss-on-ignition determinations have been made for the Bunbury Basalt (BB1). Most of these have been made in 17 batches by Geoscience Australia, with 10 analyses made by a university laboratory, and either one or two analyses carried out at six commercial laboratories. The concentration of a maximum 59 trace elements and REE have been determined by a variety of methods. The majority of analyses were made by Geoscience Australia, with additional analyses made at a university laboratory and at six commercial laboratories. There are 12 determinations for Au and 10 determinations of Pd and Pt, all carried out at commercial laboratories.

Analytical techniques at Geoscience Australia and the university laboratory comprise XRF and ICP-MS, and for five elements analysed by Geoscience Australia (Ba, Rb, Sr, Y and Zr) both XRF and ICP-MS data are available. Commercial laboratories have used XRF, ICP-

MS, and ICP-OES (ICP-optical emission spectrometry), with samples prepared using fire assay preconcentration, aqua regia digestion, multi-acid digestion, and alkaline fusion followed by acid attack. In Appendix 1 laboratory methods are reported as generic to avoid the complication of individual laboratory acronyms.

Major element oxides

The similarity of the mean and median and low skewness values for all oxide data indicate a normal distribution (Table 2). The percent relative standard deviation (RSD%; $100 \times (\text{SD}/\text{mean})$) provides a measure of precision, with values of less than 5 for SiO_2 , TiO_2 , Al_2O_3 , $\text{Fe}_2\text{O}_3\text{T}$, CaO , and FeO . RSD% values for the remaining oxides and LOI are higher, although most of these values are less than 10. Most oxides show a unimodal distribution (e.g. Fig. 3a), but MgO is bimodal (Fig. 3b); most MgO values lie between 4.4 and 5.0%, but 14 analyses from Geoscience Australia batch S200261 plot between 4.0 and 4.1, and one analysis from CL5 plots at 5.37%. If values plotting more than one standard deviation from the mean are excluded, there is only a small difference in mean values (4.56% for untrimmed data compared to 4.73% for trimmed data), but the standard deviation shrinks from 0.34 to 0.15 (compare Fig. 3c,d). This statistical trimming of these data also highlights a small but consistent difference in MgO measured by Geoscience Australia and lab UL1, although this difference is enhanced by the choice of small bin sizes for histograms.

Statistics for trimmed data (Table 3) show that between 6% (P_2O_5) and 55% (SO_3) of values were culled. Both of these oxides are at similar low levels, therefore it is difficult to ascribe their difference in precision in terms of low concentration. Predictably, trimming produces a tighter distribution for all analytes, as shown by lower RSD% values.

Trace elements, rare earth elements, and precious metals

Of the 59 trace elements and REE for which data are available (Appendix 1), statistical analysis has not been carried out for Ag, B, Bi, C, Cd, Hg, In, Pd, Pt, Re, Rh, Se, Te, Tl, and W, because more than 30% of determinations returned values of less than the lower level of detection, or there were less than 5 separate determinations. For these 15 elements, suggested values are tabulated.

Examination of available data (Appendix 1) shows that although there is a narrow range in concentrations for most elements, there are occasional extreme values (e.g. 81 ppm for Ag from one commercial laboratory, with most other analyses returning close to or less than the detection level). For some elements (e.g. As, which ranges from less than detection level to 11.1 ppm, with an average value of 5 ppm) the spread of data to lower concentrations is accounted for by single analyses from three commercial laboratories who recorded concentrations less than detection level (Fig. 4a). These data also show that analysis by XRF provides more precise data (Fig. 4b).



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Figure 2. The Bunbury Basalt (BB1) geochemical reference material at the Gelorup Quarry, east of Bunbury (Zone 50, MGA 375756E 6302681N). Photograph: S. Sheppard

Table 2. Statistics for major element oxide and LOI for all data generated on the Bunbury Basalt (BB1)

	n	Mean	Geometric mean	Median	Minimum	Maximum	Lower quartile	Upper quartile	Range	Quartile range	Variance	SD	Standard error	Skewness	Kurtosis	RSD%	Mean +1SD	Mean -1SD
										Percentage								
SiO ₂	49	51.83	51.82	51.69	50.04	53.89	51.43	52.38	3.85	0.96	0.47	0.69	0.10	0.1	1.3	1.3	52.51	51.14
TiO ₂	52	2.03	2.03	2.01	1.82	2.22	1.98	2.09	0.40	0.11	0.01	0.07	0.01	0.0	1.2	3.6	2.10	1.95
Al ₂ O ₃	52	15.40	15.40	15.33	14.88	17.89	15.24	15.41	3.01	0.17	0.20	0.45	0.06	4.3	20.9	2.9	15.85	14.95
Fe ₂ O ₃ T	52	12.24	12.24	12.23	11.88	12.60	12.12	12.40	0.72	0.28	0.03	0.17	0.02	-0.2	-0.6	1.4	12.40	12.07
MnO	52	0.16	0.16	0.16	0.12	0.20	0.16	0.17	0.08	0.01	0.00	0.01	0.00	-0.5	5.5	7.7	0.17	0.15
MgO	52	4.56	4.55	4.62	4.01	5.37	4.10	4.86	1.36	0.77	0.11	0.34	0.05	-0.3	-0.8	7.4	4.90	4.22
CaO	52	8.76	8.75	8.74	8.35	10.16	8.64	8.78	1.81	0.14	0.08	0.29	0.04	2.9	11.7	3.3	9.04	8.47
Na ₂ O	51	3.06	3.06	3.01	2.44	4.18	2.97	3.10	1.74	0.13	0.06	0.24	0.03	2.7	12.2	7.7	3.30	2.83
K ₂ O	52	0.46	0.46	0.45	0.42	0.61	0.45	0.47	0.19	0.02	0.00	0.03	0.00	3.0	10.7	7.2	0.50	0.43
P ₂ O ₅	52	0.26	0.25	0.24	0.19	0.56	0.24	0.26	0.37	0.03	0.00	0.06	0.01	4.4	20.2	23.1	0.32	0.20
SO ₃	31	0.16	0.16	0.15	0.10	0.21	0.13	0.20	0.11	0.07	0.00	0.04	0.01	-1.7	-1.7	22.6	0.20	0.13
LOI	29	1.72	1.52	1.75	0.09	2.68	1.59	2.11	2.59	0.52	0.36	0.60	0.11	-1.0	0.9	34.7	2.32	1.13
Fe ₂ O ₃	30	3.31	3.29	3.30	2.91	3.89	3.08	3.48	0.98	0.40	0.08	0.28	0.05	0.5	-0.6	8.4	3.58	3.03
FeO	30	7.98	7.97	8.03	7.57	8.35	7.83	8.16	0.78	0.33	0.05	0.21	0.04	-0.3	-0.5	2.7	8.19	7.76

NOTES:
 n: Number of samples
 SD: Standard deviation
 RSD%: Relative standard deviation ($100 \times \text{SD}/\text{Mean}$)
 LOI: Loss on ignition

Untrimmed data for elements treated statistically (Table 4) have been used to generate a series of working values and acceptable ranges (Table 5). The trimmed data for Au result in a mean Au concentration of 14.3 ppb (SD = 2.7 ppb), which is higher than that of most basaltic rocks (a basaltic rock average of 3.6 ppb Au has been reported by Wedephol, 1978). The higher average Au content of BB1 is attributed to crushing of the sample immediately following preparation of a Au-bearing reference material (Knowles, A, 2003, written comm.). A summary of working and suggested values, and an acceptable range for most analytes is shown in Table 6.

Assessing the effects of analytical technique on analyte concentrations

Analyses from Geoscience Australia include 16 measurements for Ba, Rb, Sr, Y, Pb, and Zr by both XRF and ICP-MS. Categorized histograms (Fig. 5a–f) illustrate the effects of technique on analyte concentration. The average Ba content determined by XRF (134 ppm; Fig. 5a) is lower than that determined by ICP-MS (155 ppm), although the SD for both methods is similar (close to 7 ppm). The average values for Rb (Fig. 5b) according to technique are also different (XRF = 12.6 ppm, ICP-MS = 14.7 ppm), but Rb by XRF shows a narrower range (SD = 0.38) than ICP-MS (SD = 2 ppm). The average values for Sr (Fig. 5c) and Y (Fig. 5d) by XRF are slightly higher than those by ICP-MS, but there is a narrower range in values for Sr by XRF (SD = 11 ppm) compared to ICP-MS (SD = 21 ppm), whereas SD values are similar for Y (close to 5 ppm). Average values for Zr (Fig. 5e) are almost identical (close to 150 ppm), but the SD for ICP-MS data is greater than that for XRF (8.1 vs 5.8). Due to low concentrations, some of the difference in average Pb concentrations according to method (XRF = 5.9 ppm, SD = 1.3 ppm; ICP = 4.4 ppm, SD = 1.6 ppm) could be caused by analytical issues (Fig. 5f). Thus, mean values for Ba, and to a lesser extent Rb, vary according to technique, with XRF giving lower values than ICP-MS. For all six elements the SD is greater for ICP-MS than XRF, which suggests that there may be incomplete sample dissolution in some cases prior to ICP-MS analysis.

Kerba Monzogranite (KG1)

The Kerba Monzogranite intrudes Archean granitic gneiss and granite along the southern margin of the Yarlalweelor Gneiss Complex in the western part of the Capricorn Orogen (Fig. 1). A sample of the Kerba Monzogranite has been dated at 1808 ± 6 Ma by Nelson (1998; GSWA 142851) by sensitive high-resolution ion microprobe (SHRIMP) U–Pb zircon methodology. The sample collected as a reference material is from a 4–5 m-long, 2 m-wide and 1 m-high boulder on the MOORARIE 1:100 000 map sheet (Zone 50, MGA 580875E 7172899N), which was broken up using explosives, revealing an unweathered interior (Fig. 6). The rock is a massive to weakly foliated, pale-grey, equigranular to sparsely porphyritic biotite monzogranite. About 3% of the rock

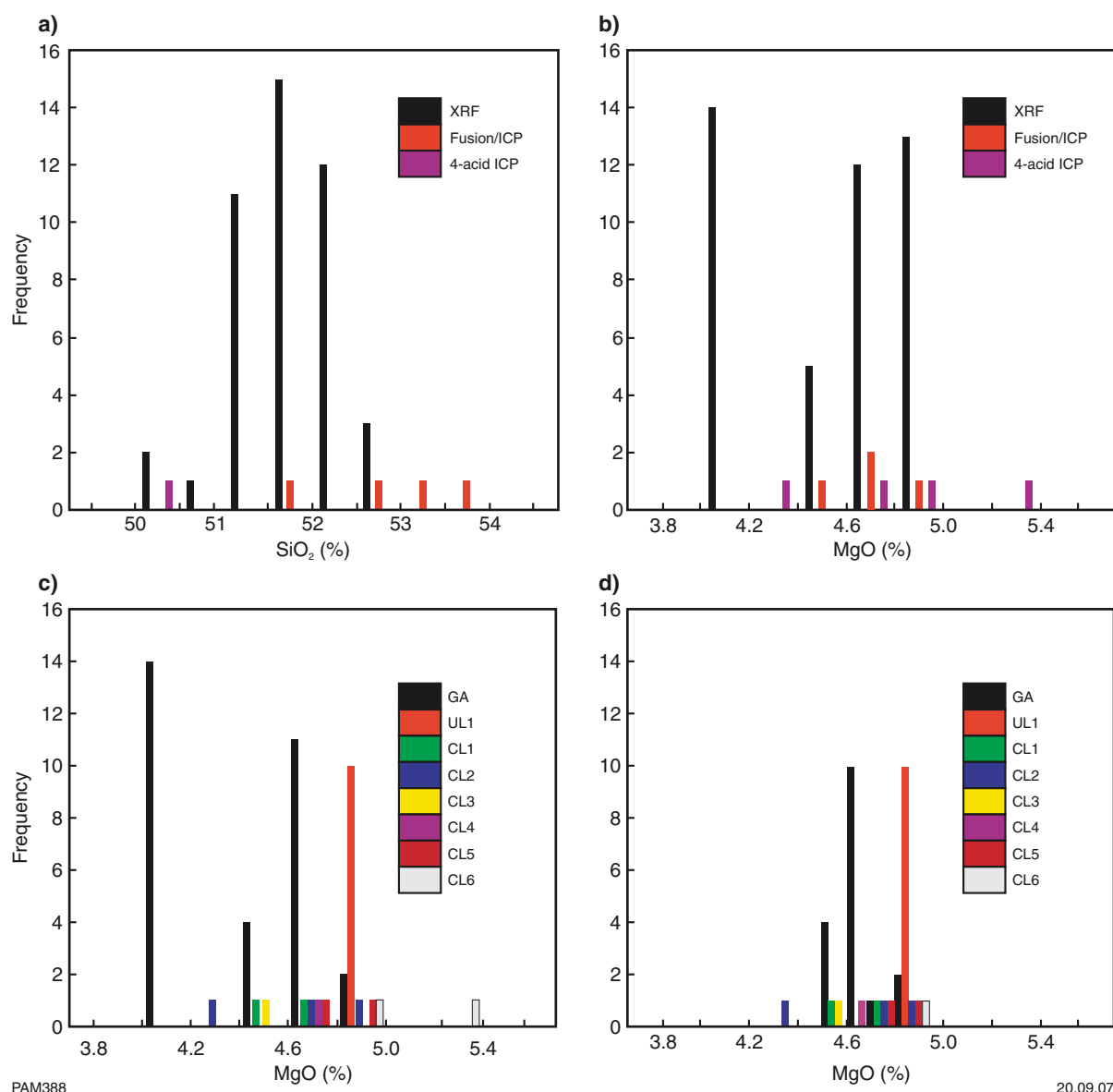


Figure 3. Frequency histograms for the Bunbury Basalt (BB1) according to generic technique: a) SiO_2 ; b) MgO ; c) untrimmed data for MgO according to laboratory; and d) trimmed data according to laboratory. GA = Geoscience Australia, UL = university laboratory, CL = commercial laboratory

is composed of 5–8 mm-long K-feldspar phenocrysts. Evidence for low-grade metamorphism is shown by the ragged nature of biotite crystals (with exsolved rutile needles), subgrain development of quartz, weak sericitization of plagioclase, and pseudomorphing of magnetite by epidote distributed throughout the rock.

Major element oxides

Of the 35 major element oxide analyses of the Kerba Monzogranite, 32 are from 18 batches analysed by Geoscience Australia, with three analyses by CL7 (Appendix 2). Summary statistics on untrimmed data (Table 7) show that most RSD% values are less than 5, but Fe_2O_3 , SO_3 , and P_2O_5 have RSD% values more than 10, and the loss on ignition (LOI) RSD% value is 89. The

wide variation for P_2O_5 and SO_3 can be attributed to poorer precision at levels close to detection. Most major element oxides and LOI show a normal distribution (e.g. Al_2O_3 ; Fig. 7a), but some show a bimodal distribution which is a byproduct of histogram bin sizes (e.g. CaO ; Fig. 7b) over a limited concentration range. Examination of raw data shows that there is no clear separation of analyte concentration in terms of laboratory.

Trimming of data by excluding all analyses that lie beyond one SD of the mean (Table 8) reduces most RSD% values to less than 3, although there are still higher values for both SO_3 (19) and LOI (51). The poorer precision for SO_3 is also seen for sample BB1, and may be due to the unsuitability of XRF for analysis of sulfur. The LOI analysis is a gravimetric technique, which may be less well constrained than either XRF or ICP.

Table 3. Statistics for trimmed data (Bunbury Basalt, BB1), major element oxides, and LOI generated from data that lie within one standard deviation of the mean for all data (Appendix 1)

	Total n	Trimmed n	% of data trimmed	Mean	Geometric mean	Median	Mini- mum	Maxi- mum	Lower quartile	Upper quartile	Range	Quartile range	Vari- ance	SD	Standard error	Skew- ness	Kurtosis	RSD%	Mean +2SD	Mean -2SD
SiO ₂	49	38	22	51.82	51.82	51.68	51.24	52.48	51.50	52.30	1.24	0.80	0.17	0.41	0.07	0.47	-1.26	0.79	52.64	51.01
TiO ₂	52	40	23	2.02	2.02	2.00	1.96	2.10	1.98	2.03	0.14	0.05	0.00	0.04	0.01	0.89	-0.25	2.03	2.10	1.93
Al ₂ O ₃	52	47	10	15.33	15.33	15.33	15.10	15.83	15.25	15.40	0.73	0.15	0.02	0.13	0.02	1.31	4.47	0.82	15.58	15.08
Fe ₂ O ₃ T	52	30	42	12.22	12.21	12.21	12.08	12.38	12.14	12.28	0.30	0.14	0.01	0.09	0.02	0.31	-0.87	0.74	12.40	12.03
MnO	52	40	23	0.16	0.16	0.16	0.15	0.17	0.16	0.17	0.02	0.01	0.00	0.01	0.00	0.54	-1.00	3.34	0.17	0.15
MgO	52	37	29	4.72	4.72	4.71	4.33	4.90	4.62	4.87	0.57	0.25	0.02	0.15	0.02	-0.44	-0.56	3.13	5.02	4.43
CaO	52	43	17	8.71	8.71	8.73	8.50	8.84	8.66	8.78	0.34	0.12	0.01	0.08	0.01	-0.75	-0.32	0.97	8.88	8.54
Na ₂ O	51	47	8	3.03	3.03	3.01	2.90	3.25	2.97	3.07	0.35	0.10	0.01	0.08	0.01	1.09	0.74	2.62	3.19	2.87
K ₂ O	52	46	12	0.46	0.45	0.45	0.44	0.49	0.45	0.46	0.05	0.02	0.00	0.01	0.00	1.05	0.45	2.76	0.48	0.43
P ₂ O ₅	52	49	6	0.25	0.25	0.24	0.21	0.27	0.24	0.26	0.06	0.03	0.00	0.01	0.00	0.10	-0.66	5.73	0.28	0.22
SO ₃	31	14	55	0.16	0.16	0.15	0.14	0.20	0.14	0.20	0.06	0.05	0.00	0.03	0.01	0.58	-1.80	16.57	0.22	0.11
LOI	29	19	34	1.81	1.80	1.75	1.48	2.26	1.61	2.05	0.78	0.44	0.06	0.24	0.05	0.33	-1.16	13.20	2.29	1.33
Fe ₂ O ₃	30	18	40	3.28	3.28	3.30	3.03	3.54	3.17	3.37	0.50	0.20	0.02	0.15	0.03	-0.03	-0.91	4.46	3.57	2.99
FeO	30	20	33	7.99	7.99	8.03	7.82	8.18	7.87	8.06	0.36	0.18	0.01	0.12	0.03	-0.07	-1.24	1.48	8.23	7.75

NOTES: n: Number of samples
SD: Standard deviation
RSD%: Relative standard deviation (100 × SD/Mean)
LOI: Loss on ignition

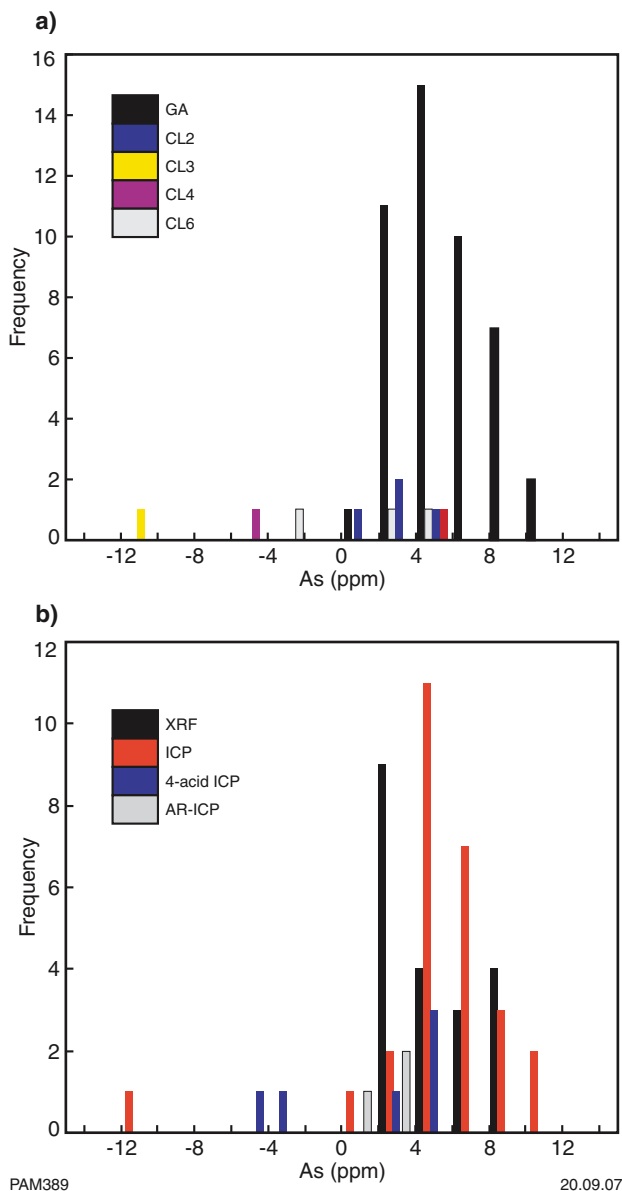


Figure 4. Frequency histograms for As for the Bunbury Basalt (BB1): a) according to laboratory; and b) generic technique. GA = Geoscience Australia, CL = commercial laboratory

Trace elements and rare earth elements

Thirty-six trace element analyses have been carried out (Appendix 2) comprising 32 analyses in 18 batches from Geoscience Australia, one from CL8, and three from CL7. Because the majority of analyses for Ag, As, Au, Bi, Cd, Pd, and Pt returned values less than the lower level of detection, these data have not been statistically treated, and only suggested values have been compiled. Statistics on untrimmed data (Table 9) show that RSD% values are less than or close to 10 for all elements apart from Cu (39), F (18), Lu (24), Mo (32), Ni (114), Sb (45), Sc (251), Sn (23), and Ta (62). The poor precision

Table 4. Statistics for trace and rare earth elements for the data generated on the Bunbury Basalt (BB1)

	<i>n</i>	Mean	Geometric mean	Median	Minimum	Maximum	Lower quartile	Upper quartile	Range	Quartile range	Variance	SD	Standard error	Skewness	Kurtosis	RSD%	Mean +1SD	Mean -1SD
As	56	5.0	—	5.4	-10.0	11.1	3.3	7.3	21.1	4.1	12.5	3.5	0.5	-1.8	5.8	71.2	8.5	1.4
Au	10	12.9	—	14.0	-0.1	17.0	12.0	17.0	17.1	5.0	27.5	5.2	1.7	-1.9	4.2	40.7	18.1	7.6
Ba	51	150	149	150	123	178	138	160	55	22	202	14	2	-0.1	-0.7	9.5	164	136
Be	41	0.7	—	0.8	-1.0	1.4	0.7	0.9	2.4	0.2	0.3	0.5	0.1	-2.4	6.1	76.7	1.2	0.2
Ce	49	26.66	26.48	27.10	13.00	36.10	25.70	27.56	23.10	1.86	7.87	2.81	0.40	-1.7	13.3	10.5	29.47	23.86
Co	11	36	36	37	32	39	34	38	7	5	6	2	1	-0.6	-1.0	6.6	39	34
Cr	44	149	148	152	112	190	143	154	78	10	167	13	2	-0.2	2.8	8.7	162	136
Cs	40	0.27	—	0.36	-3.00	0.40	0.34	0.38	3.40	0.05	0.28	0.53	0.08	-6.3	39.7	193.9	0.81	-0.26
Cu	41	80	80	81	68	89	79	84	21	5	23	5	1	-0.9	0.4	6.0	85	75
Dy	40	7.21	7.20	7.30	5.78	8.10	7.00	7.48	2.32	0.49	0.15	0.39	0.06	-1.1	3.5	5.4	7.60	6.82
Er	42	3.94	3.94	3.95	3.02	4.70	3.87	4.00	1.68	0.13	0.06	0.25	0.04	-0.7	6.1	6.2	4.19	3.70
Eu	42	2.01	2.01	2.01	1.69	2.21	1.96	2.05	0.52	0.09	0.01	0.09	0.01	-0.5	3.3	4.5	2.10	1.92
F	31	388	377	412	106	451	381	424	345	43	5222	72	13	-2.6	7.3	18.6	460	315
Ga	46	24	24	23	21	27	23	24	6	1	1	1	0	0.9	1.5	5.0	25	22
Gd	43	7.06	6.47	7.21	0.07	8.00	6.87	7.66	7.93	0.79	1.44	1.20	0.18	-4.9	28.6	17.0	8.25	5.86
Ge	34	1.6	1.5	1.5	1.2	2.9	1.4	1.6	1.7	0.2	0.1	0.3	0.1	3.0	11.8	19.3	1.9	1.3
Hf	43	4.0	4.0	4.0	3.6	4.5	3.9	4.2	0.9	0.3	0.1	0.2	0.0	-0.2	-0.6	5.6	4.2	3.8
Ho	41	1.47	1.46	1.45	1.24	1.64	1.38	1.58	0.40	0.20	0.01	0.11	0.02	-0.1	-1.2	7.8	1.58	1.35
La	44	10.93	10.91	11.00	9.46	13.00	10.56	11.20	3.54	0.65	0.42	0.65	0.10	0.6	2.4	5.9	11.57	10.28
Li	7	7.6	7.6	7.5	7.0	8.4	7.4	7.8	1.4	0.4	0.2	0.4	0.2	0.2	1.8	5.7	8.0	7.2
Lu	41	0.49	0.49	0.49	0.41	0.55	0.47	0.52	0.14	0.05	0.00	0.03	0.01	-0.3	-0.3	7.0	0.53	0.46
Mo	42	1.8	—	1.8	-2.0	5.0	1.5	2.0	7.0	0.5	0.8	0.9	0.1	-0.7	10.9	49.6	2.7	0.9
Nb	50	6.5	—	7.5	-15.0	12.4	7.2	7.7	27.4	0.5	30.4	5.5	0.8	-2.8	7.8	85.2	12.0	1.0
Nd	43	17.97	—	18.88	-15.00	21.20	18.01	19.45	36.20	1.44	27.23	5.22	0.80	-6.3	40.5	29.0	23.19	12.75
Ni	49	42	—	43	-50	186	36	47	236	11	655	26	4	2.8	24.2	60.3	68.03	16.82
Pb	64	4.3	—	4.3	-5.0	8.3	3.6	6.0	13.3	2.5	6.3	2.5	0.3	-2.3	7.0	58.6	6.8	1.8
Pr	41	3.67	3.67	3.64	3.28	4.12	3.53	3.83	0.84	0.30	0.04	0.20	0.03	0.4	-0.4	5.4	3.87	3.48
Rb	64	12.8	12.7	12.5	10.5	18.6	11.2	13.7	8.1	2.4	3.6	1.9	0.2	1.0	0.7	14.8	14.7	10.9
S	7	0.05	—	0.06	-0.04	0.07	0.05	0.07	0.11	0.01	0.00	0.04	0.01	-2.55	6.64	82.30	0.09	0.01
Sb	43	0.6	—	0.3	-5.0	6.1	0.2	0.5	11.1	0.3	2.6	1.6	0.2	0.8	6.7	279.8	2.2	-1.0
Sc	43	27.8	27.7	28.0	24.0	31.0	26.0	30.0	7.0	4.0	4.5	2.1	0.3	-0.2	-1.3	7.6	29.9	25.7
Sm	42	5.71	5.71	5.70	5.08	6.30	5.51	5.90	1.22	0.39	0.07	0.27	0.04	0.1	-0.3	4.7	5.98	5.44
Sn	43	1.3	—	1.7	-10.0	3.0	1.4	2.0	13.0	0.6	4.4	2.1	0.3	-4.5	21.4	166.1	3.4	-0.8
Sr	63	245.3	244.8	247.2	184.3	284.0	238.1	251.4	99.7	13.3	248.3	15.8	2.0	-0.9	3.6	6.4	261.06	229.54
Ta	44	0.4	—	0.5	-2.0	0.7	0.4	0.5	2.7	0.1	0.2	0.4	0.1	-4.9	27.9	109.7	0.78	-0.04
Tb	41	1.22	1.22	1.23	1.02	1.36	1.15	1.30	0.34	0.15	0.01	0.08	0.01	-0.3	-0.8	6.9	1.31	1.14
Th	48	1.8	1.8	1.8	1.3	3.0	1.6	1.9	1.7	0.3	0.1	0.3	0.0	1.6	3.4	18.2	2.2	1.5
Tm	10	0.37	—	0.51	-1.00	0.60	0.48	0.57	1.60	0.09	0.24	0.49	0.15	-3.1	9.7	129.6	0.86	-0.11
U	43	0.3	—	0.3	-0.5	0.6	0.3	0.3	1.1	0.0	0.0	0.1	0.0	-4.6	29.0	46.5	0.4	0.2
V	47	236	234	239	194	289	206	255	95	49	748	27	4	0.0	-1.3	11.6	263	209
Y	65	38.4	—	39.5	-1.0	51.1	37.1	42.0	52.1	4.9	44.8	6.7	0.8	-3.4	18.3	17.4	45.09	31.70
Yb	42	3.23	—	3.30	-1.00	4.10	3.23	3.35	5.10	0.12	0.49	0.70	0.11	-5.6	35.2	21.6	3.93	2.54
Zn	47	116.8	114.7	114.3	57.0	156.3	114.0	118.0	99.3	4.0	416.8	20.4	3.0	-0.7	3.4	17.5	137.2	96.4
Zr	61	152	152	154	129	170	146	157	42	11	71	8	1	-0.5	0.6	5.5	161	144

NOTES: n: number of samples
SD: Standard deviation
RSD%: Relative standard deviation ($100 \times \text{SD}/\text{Mean}$)

Table 5. Statistics for trimmed data (Bunbury Basalt, BB1) for trace and rare earth elements. These data have been generated by calculating statistics on all data that lie within one standard deviation of the mean for all data (Appendix 1)

	Total n	Trimmed n	% of data trimmed	Mean	Geometric mean	Median	Mini- mum	Maxi- mum	Lower quartile	Upper quartile	Range	Quartile range	Vari- ance	SD	Standard error	Skew- ness	Kurtosis	RSD%	Mean -2SD	Mean +2SD
As	56	46	18	5.2	4.8	5.2	2.0	8.4	3.3	6.3	6.4	3.0	3.4	1.8	0.3	0.1	-1.1	35.7	1.5	8.8
Au	10	9	10	14.3	14.1	14.0	9.0	17.0	13.0	17.0	8.0	4.0	7.5	2.7	0.9	-0.8	0.2	19.1	8.9	19.8
Ba	51	32	37	152	152	153	136	162	147	158	26	11	49	7	1	0	-1	5	138	166
Be	41	36	12	0.8	0.8	0.8	0.4	1.2	0.7	0.9	0.8	0.2	0.0	0.2	0.0	0.2	0.1	24.7	0.4	1.2
Ce	49	41	16	26.77	26.75	27.10	24.66	29.00	25.84	27.42	4.34	1.58	1.18	1.09	0.17	-0.22	-0.74	4.07	24.59	28.95
Co	11	7	36	37	37	37	35	39	36	38	4	2	2	1	0	-1	0	3	35	40
Cr	44	35	20	150	150	152	139	165	147	153	26	6	30	5	1	0	1	4	140	161
Cu	41	31	24	82	82	82	78	85	80	84	7	4	4	2	0	0	-1	2	78	86
Dy	40	31	23	7.27	7.27	7.32	6.82	7.60	7.06	7.48	0.78	0.42	0.05	0.22	0.04	-0.33	-1.07	3.03	6.83	7.72
Er	42	36	14	3.95	3.95	3.95	3.73	4.17	3.90	4.00	0.44	0.11	0.01	0.09	0.02	0.07	0.42	2.33	3.77	4.13
Eu	42	33	21	2.01	2.01	2.01	1.93	2.10	1.97	2.05	0.18	0.08	0.00	0.05	0.01	-0.10	-0.97	2.38	1.92	2.11
F	31	27	13	412	411	414	363	451	400	427	88	27	530	23	4	-1	0	6	366	458
Ga	46	36	22	23	23	23	22	24	23	24	2	1	0	1	0	0	-1	2	22	24
Gd	43	41	5	7.26	7.24	7.36	6.10	8.00	6.94	7.66	1.90	0.72	0.21	0.46	0.07	-0.51	-0.56	6.29	6.34	8.17
Ge	34	28	18	1.5	1.5	1.5	1.4	1.7	1.5	1.6	0.3	0.1	0.0	0.1	0.0	0.2	-0.5	5.3	1.4	1.7
Hf	43	29	33	4.0	4.1	4.1	3.8	4.2	3.9	4.1	0.4	0.2	0.0	0.1	0.0	-0.3	-1.0	3.0	3.8	4.3
Ho	41	26	37	1.46	1.46	1.44	1.37	1.58	1.39	1.53	0.21	0.14	0.01	0.08	0.02	0.46	-1.34	5.27	1.31	1.61
La	44	34	23	10.95	10.94	11.00	10.30	11.34	10.72	11.14	1.04	0.42	0.09	0.30	0.05	-0.71	-0.39	2.74	10.35	11.55
Li	7	5	29	7.55	7.55	7.50	7.39	7.80	7.40	7.67	0.41	0.27	0.03	0.18	0.08	0.68	-1.51	2.38	7.19	7.91
Lu	41	25	39	0.49	0.49	0.49	0.46	0.52	0.48	0.50	0.06	0.02	0.00	0.02	0.00	0.28	-0.58	3.35	0.46	0.52
Mo	42	39	7	1.8	1.7	1.8	1.0	2.7	1.5	2.0	1.7	0.5	0.2	0.4	0.1	0.5	0.5	22.7	1.0	2.6
Nb	50	42	16	7.6	7.6	7.5	6.9	11.9	7.3	7.7	5.0	0.4	0.6	0.8	0.1	4.4	23.6	10.2	6.1	9.2
Nd	43	42	2	18.75	18.73	18.89	16.50	21.20	18.19	19.45	4.70	1.26	0.75	0.87	0.13	-0.17	0.93	4.63	17.02	20.49
Ni	49	47	4	41	41	43	22	49	36	47	27	11	49	7	1	-1	0	17	27	55
Pb	64	54	16	4.4	4.2	4.3	2.0	6.4	3.6	5.6	4.4	2.0	1.4	1.2	0.2	-0.1	-1.0	27.1	2.0	6.8
Pr	41	30	27	3.63	3.62	3.59	3.48	3.86	3.53	3.71	0.38	0.18	0.01	0.11	0.02	0.61	-0.73	3.12	3.40	3.85
Rb	64	43	33	12.4	12.4	12.5	11.0	14.7	11.3	13.0	3.7	1.7	1.0	1.0	0.1	0.3	-0.4	7.9	10.4	14.4
Sb	43	38	12	0.3	0.3	0.3	-1.0	1.7	0.2	0.4	2.7	0.2	0.2	0.4	0.1	0.0	5.1	139.6	-0.5	1.1
Sc	43	23	47	27.7	27.7	28.0	26.0	29.8	26.8	29.0	3.8	2.2	1.7	1.3	0.3	0.1	-1.2	4.7	25.1	30.3
Sm	42	29	31	5.69	5.69	5.66	5.46	5.98	5.53	5.83	0.52	0.30	0.03	0.16	0.03	0.15	-1.46	2.84	5.37	6.02
Sn	43	40	7	1.8	1.7	1.8	1.0	3.0	1.6	2.0	2.0	0.5	0.1	0.4	0.1	0.4	2.2	21.0	1.0	2.5
Sr	63	49	22	245.2	245.1	246.6	233.0	260.7	238.4	249.9	27.7	11.5	47.7	6.9	1.0	0.3	-0.8	2.8	231.4	259.0
Ta	44	40	9	0.5	0.4	0.5	0.2	0.7	0.4	0.5	0.5	0.1	0.0	0.1	0.0	-0.9	1.0	23.5	0.2	0.7
Tb	41	27	34	1.22	1.22	1.20	1.15	1.30	1.17	1.29	0.15	0.12	0.00	0.06	0.01	0.14	-1.57	4.66	1.11	1.34
Th	48	40	17	1.8	1.8	1.8	1.5	2.0	1.6	1.9	0.5	0.3	0.0	0.2	0.0	-0.3	-1.0	8.7	1.5	2.1
Tm	10	9	10	0.53	0.53	0.51	0.47	0.60	0.49	0.57	0.14	0.08	0.00	0.05	0.02	0.52	-1.33	9.67	0.43	0.63
U	43	41	5	0.3	0.3	0.3	0.2	0.4	0.3	0.3	0.2	0.0	0.0	0.0	0.0	-0.5	5.6	11.8	0.2	0.4
V	47	22	53	245	245	249	221	262	236	253	41	17	120	11	2	-1	0	4	223	267
Y	65	58	11	39.8	39.7	40.2	33.6	44.6	38.2	42.0	11.0	3.8	8.5	2.9	0.4	-0.5	-0.5	7.3	33.9	45.6
Yb	42	40	5	3.32	3.32	3.30	2.88	3.77	3.24	3.35	0.89	0.11	0.03	0.16	0.03	0.67	2.37	4.82	3.00	3.64
Zn	47	38	19	115.5	115.5	114.0	106.0	128.0	114.0	117.0	22.0	3.0	17.0	4.1	0.7	0.8	2.3	3.6	107.3	123.8
Zr	61	47	23	153	153	154	144	160	149	157	16	8	22	5	1	-1	-1	3	143	162

NOTES:

N: number of samples

SD: Standard deviation

RSD%: Relative standard deviation ($100 \times \text{SD}/\text{Mean}$)

Table 6. Working and suggested values for the Bunbury Basalt (BB1)

	<i>n</i>	<i>Mean</i>	<i>Comment</i>	<i>Standard deviation</i>	<i>Lower acceptable</i>	<i>Upper acceptable</i>
Percentage						
SiO ₂	38	51.82	Working	0.41	51.01	52.64
TiO ₂	40	2.02	Working	0.04	1.93	2.10
Al ₂ O ₃	47	15.33	Working	0.13	15.08	15.58
Fe ₂ O ₃ T	30	12.22	Working	0.09	12.03	12.40
MnO	40	0.16	Working	0.01	0.15	0.17
MgO	37	4.72	Working	0.15	4.43	5.02
CaO	43	8.71	Working	0.08	8.54	8.88
Na ₂ O	47	3.03	Working	0.08	2.87	3.19
K ₂ O	46	0.46	Working	0.01	0.43	0.48
P ₂ O ₅	49	0.25	Working	0.01	0.22	0.28
SO ₃	14	0.16	Working	0.03	0.11	0.22
LOI	19	1.81	Working	0.24	1.33	2.29
Fe ₂ O ₃	18	3.28	Working	0.15	2.99	3.57
FeO	20	7.99	Working	0.12	7.75	8.23
Parts per million (unless otherwise indicated)						
Ag	–	0.1	Suggested	–	–	–
As	46	5.2	Working	1.8	1.5	8.8
Au (ppb)	9	14.3	Working	2.7	8.9	19.8
B	–	<50	Suggested	–	–	–
Ba	32	152	Working	7	138	166
Be	36	0.8	Working	0.2	0.4	1.2
Bi	–	<0.1	Suggested	–	–	–
C	–	0.03	Suggested	–	–	–
Cd	–	<0.05	Suggested	–	–	–
Ce	41	26.8	Working	1.09	24.6	28.9
Co	7	37	Working	1	34.69	39.60
Cr	35	150	Working	5	140	161
Cs	–	?	–	–	–	–
Cu	31	82	Working	2	78	86
Dy	31	7.27	Working	0.22	6.83	7.72
Er	36	3.95	Working	0.09	3.77	4.13
Eu	33	2.01	Working	0.05	1.92	2.11
F	27	412	Working	23	366	458
Ga	36	23	Working	1	22	24
Gd	41	7.26	Working	0.46	6.34	8.17
Ge	28	1.5	Working	0.1	1.4	1.7
Hf	29	4.0	Working	0.1	3.8	4.3
Hg	–	<0.01	Suggested	–	–	–
Ho	26	1.46	Working	0.08	1.31	1.61
In	–	0.1	Suggested	–	–	–
La	34	10.95	Working	0.30	10.35	11.55
Li	5	7.6	Working	0.2	7.2	7.9
Lu	25	0.49	Working	0.02	0.46	0.52
Mo	39	1.8	Working	0.4	1.0	2.6
Nb	42	7.6	Working	0.8	6.05	9.16
Nd	42	18.75	Working	0.87	17.02	20.49
Ni	47	41	Working	7	27	55
Pb	54	4.4	Working	1.2	2.0	6.8
Pd (ppb)	–	<0.2	Suggested	–	–	–
Pr	30	3.63	Working	0.11	3.40	3.85
Pt (ppb)	–	<1	Suggested	–	–	–
Rb	43	12.4	Working	1.0	10.4	14.4
Re (ppb)	–	<0.01	Suggested	–	–	–
Rh (ppb)	–	<0.05	Suggested	–	–	–
Sb	38	0.3	Working	0.4	-0.5	1.1
Sc	23	27.7	Working	1.3	25.1	30.3
Se	–	<0.5	Suggested	–	–	–
Sm	29	5.69	Working	0.16	5.37	6.02
Sn	40	1.8	Working	0.4	1.0	2.5
Sr	49	245	Working	6.9	231	259
Ta	40	0.5	Working	0.1	0.2	0.7
Te	–	<0.1	Suggested	–	–	–
Tb	27	1.22	Working	0.06	1.11	1.34
Th	40	1.8	Working	0.2	1.5	2.1
Tl	–	<0.1	Suggested	–	–	–
Tm	9	0.53	Working	0.05	0.43	0.63
U	41	0.3	Working	0.0	0.2	0.4
V	22	245	Working	11	223	267
W	11	<0.3	Suggested	1.0	–	–
Y	58	39.8	Working	2.9	33.9	45.6
Yb	40	3.32	Working	0.16	3.00	3.64
Zn	38	116	Working	4.1	107	124
Zr	47	153	Working	5	143	162

NOTES: n: Number of samples

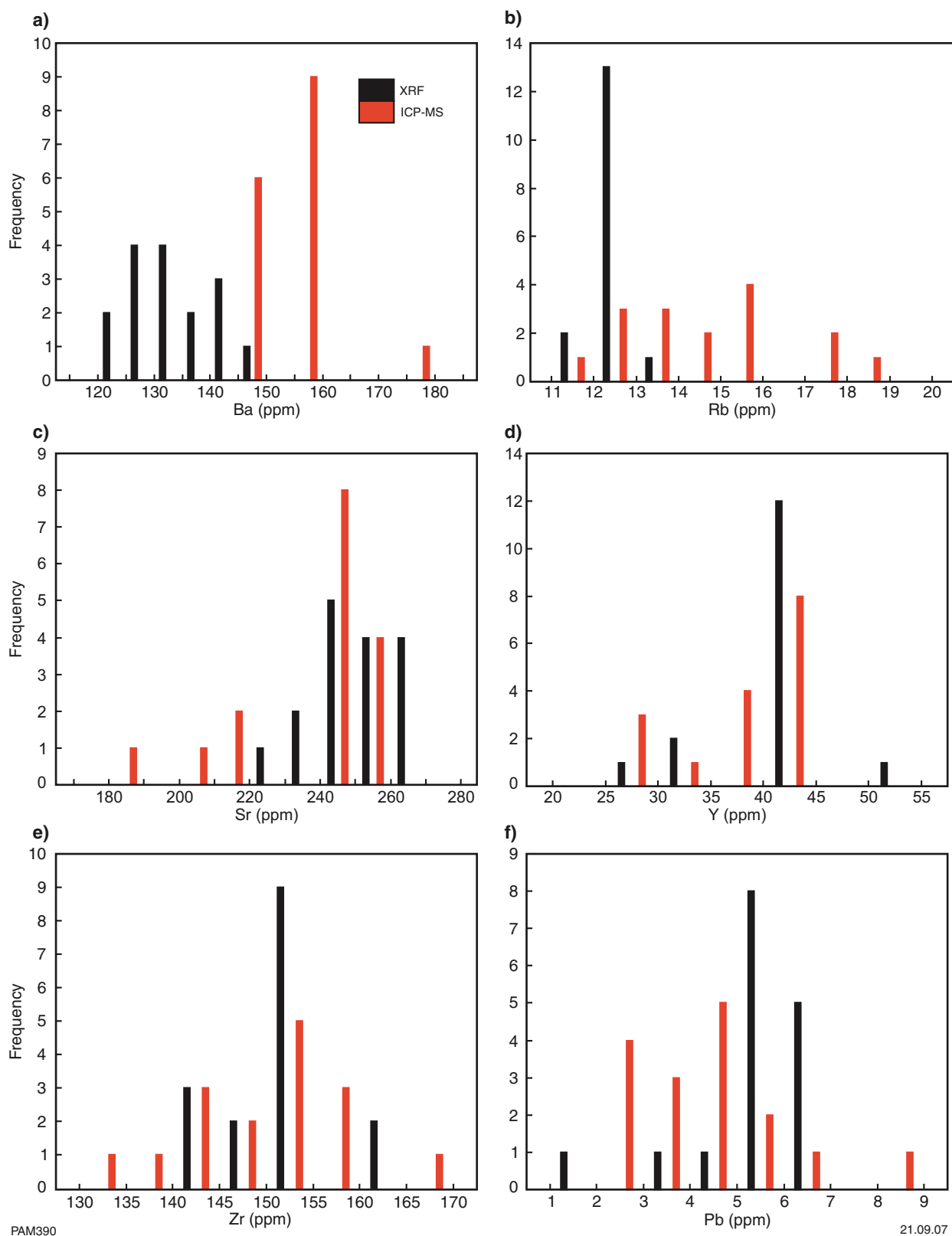


Figure 5. Frequency histograms according to method for the Bunbury Basalt (BB1) for: a) Ba; b) Rb; c) Sr; d) Y; e) Zr; and f) Pb. Data generated by Geoscience Australia



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Figure 6. The Kerba Monzogranite (KG1) geochemical reference material in the Capricorn Orogen (Zone 50, MGA 580875E 7172899N). Hammer is 33 cm long

(i.e. relatively high RSD%) of some of these elements can be accounted for by average concentrations close to the respective detection levels. There is no clear separation in terms of element concentrations according to laboratory (Fig. 7c–e), although examination of raw data (Appendix 2) shows some between-batch variations in Ni for analysis by Geoscience Australia, and Cr shows a bimodal distribution. This bimodality produces poor precision, yet the Cr concentration is well above the detection level; it is possible that the poor precision is due to the inhomogeneous distribution of a Cr-bearing mineral phase. Gold concentrations range from 5 to 47 ppb, and within one commercial laboratory, from 11 to 47 ppb. Pd concentrations range from less than 0.16 to 2 ppb, whereas Pt ranges from less than 1 to 10.73 ppb. These data indicate that gold and PGEs also appear to be inhomogeneously distributed in this monzogranite.

Assessing the effects of technique on analyte concentrations

Geoscience Australia data for six trace elements (Ba, Pb, Rb, Sr, Y, and Zr) have been determined by both ICP and XRF (Fig. 8). The data generated by ICP-MS analysis shows lower levels of precision (i.e. higher SD) for all elements apart from Pb compared to data generated by XRF, similar to data for BB1. In some cases mean values according to technique are similar, but the mean XRF and ICP-MS values for Ba (1369 and 1426 ppm) and Sr (511 and 529 ppm) are different. Average Pb concentrations are identical for both methods (39.8 ppm), with a slight difference in SD (4.0 compared to 2.3 ppm for XRF).

Statistics for trimmed data are shown in Table 10. The amount of data trimmed in generating these statistics ranges from 14% for Sr through to 56% for Ni. Inspection

Table 7. Statistics for major element oxide and LOI for all data generated on the Kerba Monzogranite (KG1)

	n	Mean	Geometric mean	Median	Minimum	Maximum	Lower quartile	Upper quartile	Range	Quartile range	Variance	SD	Standard error	Skewness	Kurtosis	RSD%	Mean +1SD	Mean -1SD
SiO ₂	35	71.27	71.26	71.40	69.52	72.13	70.94	71.64	2.61	0.70	0.28	0.53	0.09	-1.00	1.95	0.74	71.79	70.74
TiO ₂	35	0.24	0.24	0.24	0.23	0.27	0.24	0.26	0.04	0.02	0.00	0.01	0.00	0.35	-1.20	5.23	0.26	0.23
Al ₂ O ₃	35	14.96	14.96	14.97	14.55	15.20	14.89	15.05	0.65	0.16	0.02	0.13	0.02	-0.74	2.08	0.86	15.09	14.84
Fe ₂ O ₃ T	35	2.08	2.08	2.08	2.03	2.13	2.06	2.09	0.09	0.03	0.00	0.02	0.00	-0.03	-0.02	1.10	2.10	2.06
MnO	35	0.04	0.04	0.04	0.03	0.04	0.04	0.04	0.01	0.00	0.00	0.00	0.00	-0.14	-0.46	4.46	0.04	0.04
MgO	35	0.48	0.48	0.48	0.46	0.56	0.47	0.49	0.10	0.02	0.00	0.02	0.00	3.02	9.75	4.37	0.50	0.46
CaO	34	2.16	2.16	2.16	2.07	2.23	2.13	2.20	0.16	0.07	0.00	0.04	0.01	-0.07	-0.69	1.85	2.20	2.12
Na ₂ O	35	4.08	4.08	4.07	3.98	4.22	4.03	4.11	0.25	0.08	0.00	0.06	0.01	0.69	-0.12	1.48	4.14	4.02
K ₂ O	35	3.47	3.47	3.47	3.33	3.54	3.45	3.50	0.21	0.06	0.00	0.04	0.01	-0.72	2.38	1.15	3.51	3.43
P ₂ O ₅	35	0.08	0.08	0.08	0.06	0.09	0.07	0.09	0.03	0.02	0.00	0.01	0.00	0.20	-1.39	11.31	0.09	0.07
SO ₃	32	0.03	0.03	0.03	0.01	0.05	0.03	0.04	0.04	0.01	0.00	0.01	0.00	-1.04	1.07	28.02	0.04	0.02
LOI	35	0.83	-	0.63	-0.32	3.29	0.35	1.40	3.60	1.05	0.54	0.74	0.12	1.06	2.20	89.22	1.56	0.09
Fe ₂ O ₃	31	0.62	0.62	0.65	0.41	0.74	0.58	0.69	0.32	0.12	0.01	0.09	0.02	-0.93	0.07	14.03	0.71	0.54
FeO	33	1.31	1.31	1.30	1.22	1.49	1.26	1.32	0.27	0.06	0.01	0.08	0.01	1.23	0.60	5.83	1.39	1.24

NOTES:
n: Number of samples
SD: Standard deviation
RSD%: Relative standard deviation (100 × SD/Mean)
LOI: Loss on ignition

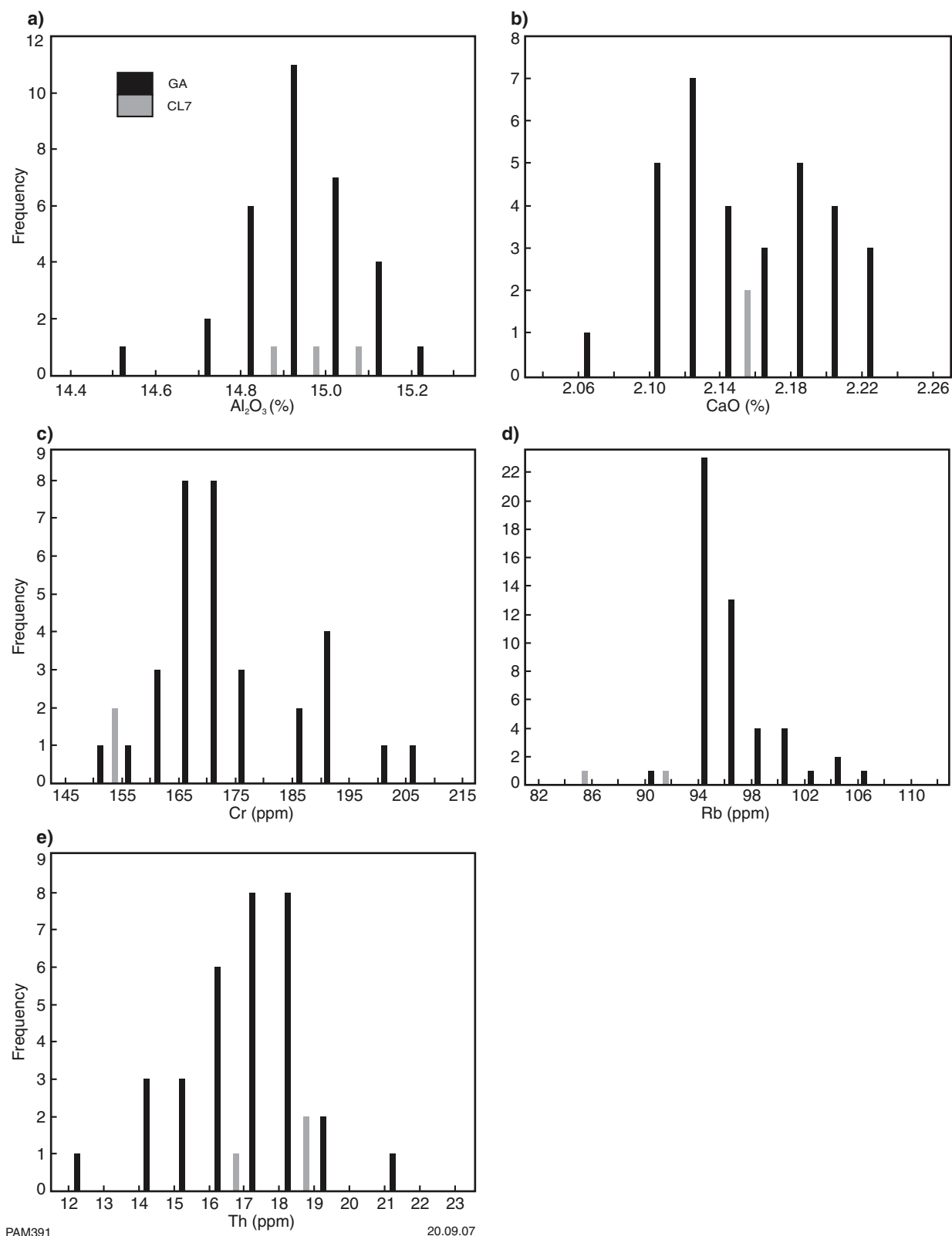


Figure 7. Frequency histograms according to laboratory for the Kerba Monzogranite (KG1): a) Al_2O_3 ; b) CaO; c) Cr; d) Rb; and e) Th

Table 8. Statistics for trimmed data (Kerba Monzogranite, KG1), major element oxides and LOI generated from data that lie within one standard deviation of the mean for all data (Appendix 2)

Total n	Trimmed n	% of data trimmed	Mean	Geometric mean	Median	Mini- mum	Maxi- mum	Lower quartile	Upper quartile	Range	Quartile range	Vari- ance	SD	Standard error	Skew- ness	Kurtosis	RSD%	Mean -2SD	Mean +2SD
35	26	26	71.37	71.36	71.44	70.75	71.78	71.08	71.64	1.03	0.56	0.10	0.32	0.06	-0.5	-1.0	0.4	70.73	72.01
35	26	26	0.24	0.24	0.24	0.23	0.26	0.24	0.25	0.03	0.02	0.00	0.01	0.00	0.4	-1.3	3.9	0.22	0.26
35	24	31	14.95	14.95	14.94	14.86	15.09	14.90	15.00	0.23	0.10	0.00	0.06	0.01	0.3	-0.6	0.4	14.83	15.07
35	22	37	2.08	2.08	2.08	2.06	2.10	2.07	2.09	0.04	0.02	0.00	0.01	0.00	0.2	-1.0	0.5	2.06	2.10
35	35	0	0.04	0.04	0.04	0.03	0.04	0.04	0.04	0.01	0.00	0.00	0.00	0.00	-0.1	-0.5	4.5	0.03	0.04
35	33	6	0.48	0.48	0.48	0.46	0.49	0.47	0.48	0.03	0.01	0.00	0.01	0.00	0.4	-0.7	1.8	0.46	0.49
34	21	38	2.16	2.16	2.16	2.13	2.20	2.14	2.18	0.07	0.04	0.00	0.02	0.01	0.2	-1.4	1.1	2.11	2.21
35	22	37	4.07	4.07	4.06	4.03	4.13	4.04	4.09	0.10	0.04	0.00	0.03	0.01	0.7	0.0	0.6	4.01	4.12
35	24	31	3.47	3.47	3.46	3.44	3.51	3.45	3.48	0.07	0.03	0.00	0.02	0.00	0.5	-0.8	0.6	3.42	3.51
35	22	37	0.08	0.08	0.08	0.07	0.09	0.07	0.09	0.02	0.01	0.00	0.01	0.00	0.4	-1.5	8.5	0.07	0.09
32	28	13	0.03	0.03	0.03	0.02	0.04	0.03	0.04	0.02	0.01	0.00	0.01	0.00	-0.5	-1.1	19.3	0.02	0.04
35	26	26	0.86	0.75	0.71	0.19	1.53	0.50	1.36	1.34	0.86	0.19	0.44	0.09	0.3	-1.4	51.0	-0.02	1.74
31	21	32	0.65	0.65	0.65	0.56	0.70	0.62	0.68	0.14	0.06	0.00	0.04	0.01	-0.3	-0.5	6.2	0.57	0.73
33	24	27	1.29	1.29	1.30	1.24	1.37	1.26	1.31	0.13	0.05	0.00	0.03	0.01	0.7	0.2	2.6	1.23	1.36

NOTES:
n: Number of samples
SD: Standard deviation
RSD: Relative standard deviation ($100 \times \text{SD}/\text{Mean}$)
LOI: Loss on ignition

of these data show that the highest amount of culled data is not necessarily from elements at low concentration (i.e. potentially poorer precision), as shown for Ge (average = 0.9 ppm), for which only 16% of data have been culled. Working and suggested values, and the range of acceptable values, are presented in Table 11.

Discussion

The working and suggested values and acceptable data ranges for both BB1 and KG1 (Tables 6 and 11) provide a basis for assessment of silicate rock geochemistry, but also show the need for more analysis, particularly of Au and PGE. Because most samples analysed by Geoscience Australia are prepared in tungsten-carbide mill heads, this laboratory — which has provided the bulk of data for both BB1 and KG1 — does not provide analytical data for Co and W. Both of these elements require characterization.

Currently available data have highlighted the inhomogeneous distribution of Au, Pd, and Pt in KG1. The apparent low levels of these elements in both reference materials means that it will be necessary to use techniques and laboratories that offer precise and accurate analysis at sub-ppb level (e.g. Richardson and Burnham, 2003). In addition, there is poor precision for both Cr and Ni in KG1, which may also be due to inhomogeneous distribution of accessory mineral phases. Sample inhomogeneity issues have not been encountered for the Bunbury Basalt (BB1), therefore it is unlikely that inhomogeneity is the result of poor mixing of the sample following milling.

Because most of the data for both reference materials have been generated by Geoscience Australia, there are few data for several trace elements, including C, Cd, Hg, In, Tl, and Se. Future work must also include determination of analyte concentrations by other than a 'total' analytical approach, which has been used for most of the data generated for this Record. The acquisition of more data should also help in resolving issues related to technique-specific analysis producing different analyte concentrations (e.g. Ba and Sr by ICP-MS and XRF in KG1; Ba and Rb according to technique in BB1). The current data show that it is necessary to be aware that there can be systematic technique-specific differences in element concentrations.

Although there are few data available, those discussed above show that XRF analysis provides the most precise data for major element oxides and some trace elements, with outliers for major elements usually attributable to analysis by fusion \pm acid attack and ICP analysis by commercial laboratories. Geoscience Australia has attempted to overcome these issues by analysing the XRF-fused glass disc by ICP (Pyke, 2000).

Table 9. Statistics for trace and rare earth elements for all data generated on the Kerba Monzogranite (KG1)

	n	Mean	Geometric mean	Median	Minimum	Maximum	Lower quartile	Upper quartile	Range	Quartile range	Variance	SD	Standard error	Skewness	Kurtosis	RSD%	Mean -1SD	Mean +1SD
Ba	51	1390	1389	1371	1314	1590	1352	1418	276	66	3029	55	8	2	3	4	1335	1445
Be	16	2.5	2.4	2.5	2.0	2.9	2.3	2.6	0.9	0.4	0.1	0.3	0.1	-0.3	-0.5	10.2	2.2	2.7
Ce	34	70.5	70.3	71.2	60.2	78.8	66.8	73.7	18.6	6.8	20.2	4.5	0.8	-0.6	-0.3	6.4	66.0	75.0
Cr	34	175	174	171	155	207	167	178	52	11	176	13	2	1	0	8	161	188
Cs	34	2.2	2.2	2.2	1.9	2.4	2.0	2.3	0.6	0.3	0.0	0.2	0.0	-0.2	-0.6	7.3	2.0	2.3
Cu	34	6.0	-	6.0	-1.0	9.0	5.0	8.0	10.0	3.0	5.5	2.3	0.4	-0.9	1.1	38.9	3.7	8.3
Dy	34	0.8	0.8	0.8	0.7	0.9	0.8	0.9	0.2	0.0	0.0	0.1	0.0	-0.5	1.0	6.2	0.8	0.9
Er	34	0.4	0.4	0.4	0.4	0.5	0.4	0.5	0.1	0.0	0.0	0.0	0.0	0.3	-0.5	5.5	0.4	0.4
Eu	34	0.8	0.8	0.8	0.7	0.9	0.7	0.8	0.2	0.0	0.0	0.0	0.0	0.8	1.5	4.8	0.7	0.8
F	32	519	511	460	349	659	442	623	310	181	9162	96	17	0	-2	18	423	615
Ga	34	20	20	20	17	21	19	20	4	1	1	1	0	-1	4	4	19	20
Gd	34	1.5	1.5	1.5	1.3	1.6	1.4	1.5	0.4	0.2	0.0	0.1	0.0	-0.1	-1.0	6.9	1.4	1.6
Ge	32	0.9	0.9	0.9	0.7	1.3	0.8	1.0	0.6	0.2	0.0	0.1	0.0	1.1	1.5	14.2	0.8	1.0
Hf	34	5.0	5.0	5.0	4.3	6.2	4.8	5.3	1.9	0.5	0.2	0.4	0.1	0.8	1.2	8.1	4.6	5.5
Ho	34	0.1	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.0	0.0	0.0	0.0	-2.2	5.9	13.8	0.1	0.2
La	34	43.2	43.1	43.7	36.2	46.4	42.4	44.5	10.2	2.1	5.1	2.3	0.4	-1.4	2.3	5.2	40.9	45.5
Lu	34	0.1	-	0.1	0.0	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	-3.4	16.0	24.2	0.0	0.1
Mo	34	1.8	1.7	1.6	1.2	3.4	1.4	2.2	2.2	0.8	0.3	0.6	0.1	1.4	1.7	31.6	1.2	2.4
Nb	34	9.5	9.5	9.4	8.6	10.4	9.3	9.7	1.8	0.4	0.2	0.4	0.1	0.6	0.5	4.3	9.1	9.9
Nd	34	22.4	22.4	22.4	19.7	23.8	21.7	23.2	4.1	1.6	1.0	1.0	0.2	-0.5	0.0	4.4	21.4	23.4
Ni	34	5	-	8	-2	11	-2	10	13	12	33	6	1	0	-2	11.4	-1	11
Pb	51	40	40	40	33	52	38	41	19	3	12	3	0	1	5	9	36	43
Pr	34	6.7	6.7	6.6	6.3	7.5	6.4	6.9	1.2	0.5	0.1	0.3	0.1	0.9	0.0	5.1	6.4	7.0
Rb	51	97	97	96	86	108	95	98	22	3	13	4	1	1	3	4	93	100
Sb	34	4.3	4.1	3.6	2.8	9.1	3.4	3.8	6.3	0.4	3.8	1.9	0.3	1.9	2.0	44.7	2.4	6.3
Sc	34	0.9	-	2.0	-2.0	4.0	-2.0	3.0	6.0	5.0	4.9	2.2	0.4	-0.5	-1.6	250.7	-1.3	3.1
Sm	34	2.8	2.8	2.8	2.4	3.2	2.7	2.9	0.8	0.1	0.0	0.2	0.0	-0.1	1.2	5.5	2.7	3.0
Sn	34	1.9	1.9	1.8	1.2	3.3	1.7	2.0	2.1	0.3	0.2	0.4	0.1	1.5	2.7	23.4	1.5	2.3
Sr	51	518	517	528	411	585	493	536	173	43	964	31	4	0	2	6	487	549
Ta	34	1.1	-	1.0	-0.1	4.2	0.9	1.1	4.3	0.2	0.4	0.7	0.1	3.1	15.9	61.6	0.4	1.7
Tb	34	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.0	0.0	0.0	0.0	-0.6	2.3	12.1	0.1	0.2
Th	35	17.3	17.2	17.3	13.0	22.0	16.6	18.1	9.0	1.5	2.8	1.7	0.3	-0.1	1.8	9.6	15.6	18.9
U	35	4.1	4.1	4.2	3.6	4.8	3.9	4.3	1.3	0.5	0.1	0.3	0.0	0.2	-0.3	6.8	3.8	4.4
V	34	15	15	15	12	22	14	16	10	2	5	2	0	2	3	14	13	17
Y	51	4.5	4.5	4.5	3.1	6.2	4.0	5.0	3.1	1.0	0.3	0.5	0.1	0.3	1.0	11.8	4.0	5.0
Yb	34	0.5	0.5	0.5	0.4	0.6	0.5	0.5	0.2	0.0	0.0	0.0	0.0	0.0	2.9	6.5	0.4	0.5
Zn	34	41	40	41	30	50	37	44	20	7	19	4	1	0	0	11	36	45
Zr	51	189	189	189	165	213	186	194	48	8	72	8	1	0	2	4	180	197

NOTES: n: Number of samples
SD: Standard deviation
RSD%: Relative standard deviation ($100 \times \text{SD}/\text{Mean}$)

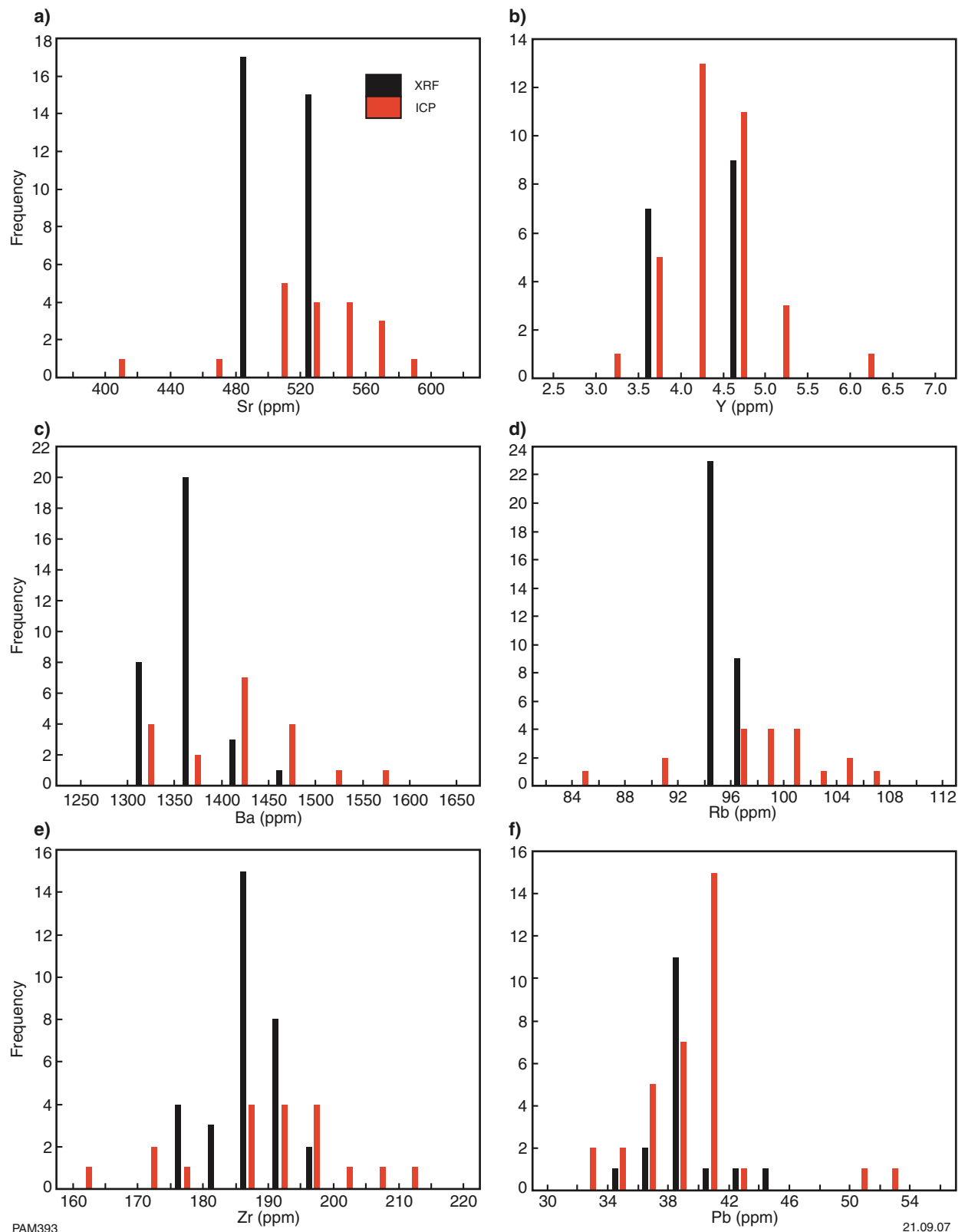


Figure 8. Frequency histograms for the Kerba Monzogranite (KG1) according to technique: a) Sr; b) Y; c) Ba; d) Rb; e) Zr; and f) Pb

Table 10. Statistics for trimmed data (Kerba Monzogranite, KG1), trace and rare earth elements. These data have been generated by calculating statistics on all data that lie within one standard deviation of the mean for all data (Appendix 2)

	Total n	Trimmed n	% of data trimmed	Mean	Geometric mean	Median	Mini- mum	Maxi- mum	Lower quartile	Upper quartile	Range	Quartile range	Vari- ance	SD	Standard error	Skew- ness	Kurtosis	RSD%	Mean -2SD	Mean +2SD
Ba	51	39	24	1373	1372	1368	1337	1431	1352	1390	94	38	718.0	26.8	4.3	0.7	-0.6	2	1346	1399
Be	16	9	44	2.5	2.5	2.5	2.3	2.6	2.5	2.6	0.3	0.1	0.0	0.1	0.0	-1.0	0.8	4	2.4	2.6
Ce	34	24	29	71.3	71.3	71.9	66.2	74.7	69.3	73.6	8.6	4.2	7.0	2.6	0.5	-0.6	-0.8	4	68.7	74.0
Cr	34	22	35	170	170	171	164	178	167	173	14	6	16.3	4.0	0.9	0.3	-0.5	2	166	174
Cs	34	24	29	2.2	2.2	2.2	2.0	2.3	2.1	2.3	0.3	0.2	0.0	0.1	0.0	-0.2	-1.4	5	2.1	2.3
Cu	34	28	18	6.2	6.0	6.0	4.0	8.0	5.0	8.0	4.0	3.0	2.5	1.6	0.3	0.0	-1.8	26	4.6	7.8
Dy	34	26	24	0.8	0.8	0.8	0.8	0.9	0.8	0.8	0.1	0.0	0.0	0.0	0.0	-0.3	-0.4	3	0.8	0.8
Er	34	17	50	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.0	0.0	0.0	0.0	0.0	0.4	-1.1	2	0.4	0.4
Eu	34	24	29	0.8	0.8	0.8	0.7	0.8	0.7	0.8	0.1	0.0	0.0	0.0	0.0	0.2	-0.6	2	0.7	0.8
F	32	20	38	484	480	452	429	610	442	520	181	78	4412	66	15	1.2	-0.3	14	417	550
Ga	34	28	18	20	20	20	19	20	19	20	1	1	0	0	0	-0.3	-1.5	2	19	20
Gd	34	19	44	1.5	1.5	1.5	1.4	1.6	1.4	1.5	0.2	0.1	0.0	0.1	0.0	-0.7	0.0	3	1.4	1.5
Ge	32	16	50	0.9	0.9	0.9	0.8	1.0	0.8	0.9	0.2	0.1	0.0	0.1	0.0	0.3	-1.2	9	0.8	1.0
Hf	34	27	21	5.0	5.0	4.9	4.7	5.4	4.8	5.2	0.7	0.4	0.1	0.2	0.0	0.3	-1.3	5	4.8	5.2
Ho	34	28	18	0.1	0.1	0.2	0.1	0.2	0.1	0.2	0.0	0.0	0.0	0.0	0.0	-0.5	-0.8	6	0.1	0.2
La	34	25	26	43.8	43.8	44.2	42.2	45.1	43.0	44.4	2.9	1.4	0.8	0.9	0.2	-0.3	-1.2	2	42.9	44.7
Lu	34	29	15	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	-0.5	-0.6	11	0.1	0.1
Mo	34	27	21	1.7	1.6	1.6	1.3	2.3	1.4	1.8	1.0	0.4	0.1	0.3	0.1	0.8	-0.5	20	1.3	2.0
Nb	34	25	26	9.5	9.5	9.4	9.2	9.9	9.3	9.5	0.7	0.2	0.0	0.2	0.0	1.1	0.5	2	9.3	9.7
Nd	34	21	38	22.4	22.4	22.3	21.5	23.4	22.1	22.9	1.9	0.9	0.4	0.6	0.1	0.0	-1.1	3	21.8	23.0
Ni	34	15	56	8	7	10	1	10	5	10	9	5	9	3	1	-1.2	0.1	39	5	11
Pb	51	43	16	40	40	40	37	43	39	41	7	2	3	2	0	-0.1	-0.5	4	38	41
Pr	34	26	24	6.6	6.6	6.6	6.4	7.0	6.4	6.8	0.7	0.3	0.0	0.2	0.0	0.6	-0.8	3	6.4	6.8
Rb	51	41	20	96	96	96	94	100	95	97	6	2	2	2	0	0.7	-0.1	2	95	98
Sb	34	29	15	3.6	3.5	3.6	2.8	5.9	3.4	3.7	3.1	0.3	0.3	0.6	0.1	2.5	10.0	16	3.0	4.1
Sc	34	21	38	2.4	2.3	2.0	2.0	3.0	2.0	3.0	1.0	1.0	0.2	0.5	0.1	0.5	-1.9	21	2	3
Sm	34	24	29	2.8	2.8	2.8	2.7	2.9	2.7	2.9	0.2	0.1	0.0	0.1	0.0	0.1	-1.0	2	2.7	2.9
Sn	34	26	24	1.8	1.8	1.8	1.5	2.0	1.7	2.0	0.5	0.3	0.0	0.2	0.0	-0.4	-1.0	10	1.6	2.0
Sr	51	44	14	515	515	521	490	548	493	534	58	41	423	21	3	0.0	-1.8	4	495	536
Ta	34	29	15	1.0	1.0	1.0	0.6	1.2	0.9	1.1	0.6	0.2	0.0	0.1	0.0	-1.0	0.6	15	0.8	1.1
Tb	34	27	21	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.0	0.0	0.0	0.0	0.0	0.6	-0.4	6	0.2	0.2
Th	35	27	23	17.4	17.4	17.3	15.9	18.5	16.7	18.1	2.6	1.4	0.6	0.8	0.1	-0.3	-0.9	4	16.7	18.2
U	35	22	37	4.2	4.2	4.2	3.9	4.4	4.0	4.3	0.5	0.4	0.0	0.2	0.0	-0.2	-1.4	4	4.0	4.3
V	34	29	15	14.6	14.5	15.0	13.0	16.0	14.0	15.0	3.0	1.0	0.9	0.9	0.2	0.0	-0.8	7	13.6	15.5
Y	51	42	18	4.5	4.5	4.5	4.0	5.0	4.1	4.9	1.0	0.8	0.1	0.4	0.1	0.1	-1.5	9	4.1	4.9
Yb	34	25	26	0.5	0.5	0.5	0.4	0.5	0.5	0.5	0.0	0.0	0.0	0.0	0.0	0.0	-1.0	3	0.4	0.5
Zn	34	26	24	41	41	41	37	44	38	44	7	6	9	3	1	-0.2	-1.8	7	38	44
Zr	51	39	24	190	190	190	181	197	186	193	16	7	15	4	1	0.0	-0.7	2	186	194

NOTES: n: Number of samples
SD: Standard deviation
RSD%: Relative standard deviation ($100 \times \text{SD}/\text{Mean}$)

Table 11. Working and suggested values for the Kerba Monzogranite (KG1)

	<i>n</i>	<i>Mean</i>	<i>Comment</i>	<i>Std dev.</i>	<i>Lower acceptable</i>	<i>Higher acceptable</i>
Percentage						
SiO ₂	26	71.37	Working	0.32	70.73	72.01
TiO ₂	26	0.24	Working	0.01	0.22	0.26
Al ₂ O ₃	24	14.95	Working	0.06	14.83	15.07
Fe ₂ O ₃ T	22	2.08	Working	0.01	2.06	2.10
MnO	35	0.04	Working	0.00	0.03	0.04
MgO	33	0.48	Working	0.01	0.46	0.49
CaO	21	2.16	Working	0.02	2.11	2.21
Na ₂ O	22	4.07	Working	0.03	4.01	4.12
K ₂ O	24	3.47	Working	0.02	3.42	3.51
P ₂ O ₅	22	0.08	Working	0.01	0.07	0.09
SO ₃	28	0.03	Working	0.01	0.02	0.04
LOI	26	0.86	Working	0.44	-0.02	1.74
Fe ₂ O ₃	21	0.65	Working	0.04	0.57	0.73
FeO	24	1.29	Working	0.03	1.23	1.36
Parts per million (unless otherwise indicated)						
Ag	—	0.01	Suggested	—	—	—
As	—	1	Suggested	—	—	—
Au (ppb)	—	5	Suggested	—	—	—
B	—	nd	Suggested	—	—	—
Ba	39	1373	Working	26.8	1346	1399
Be	9	2.5	Working	0.1	2.4	2.6
Bi	—	2	Suggested	—	—	—
C	—	—	nd	—	—	—
Cd	—	<0.1	Suggested	—	—	—
Ce	24	71.3	Working	2.6	68.7	74.0
Co	—	nd	—	—	—	—
Cr	22	170	Working	4.0	166	174
Cs	24	2.2	Working	0.1	2.1	2.3
Cu	28	6.2	Working	1.6	4.6	7.8
Dy	26	0.8	Working	0.0	0.8	0.8
Er	17	0.4	Working	0.0	0.4	0.4
Eu	24	0.8	Working	0.0	0.7	0.8
F	20	484	Working	66	417	550
Ga	28	20	Working	0	19	20
Gd	19	1.5	Working	0.1	1.4	1.5
Ge	27	0.9	Working	0.1	0.8	1.0
Hf	27	5.0	Working	0.2	4.8	5.2
Hg	—	nd	—	—	—	—
Ho	28	0.1	Working	0.0	0.1	0.2
In	—	nd	—	—	—	—
La	25	43.8	Working	0.9	42.9	44.7
Li	—	nd	—	—	—	—
Lu	29	0.1	Working	0.0	0.1	0.1
Mo	27	1.7	Working	0.3	1.3	2.0
Nb	25	9.5	Working	0.2	9.3	9.7
Nd	21	22.4	Working	0.6	21.8	23.0
Ni	15	8	Working	3	5	11
Pb	43	40	Working	2	38	41
Pd (ppb)	—	<1	Suggested	—	—	—
Pr	26	6.6	Working	0.2	6.4	6.8
Pt (ppb)	—	<1	Suggested	—	—	—
Rb	41	96	—	2	95	98
Re (ppb)	—	nd	—	—	—	—
Rh (ppb)	—	nd	—	—	—	—
Sb	29	3.6	Working	0.6	3.0	4.1
Sc	21	2.4	Working	0.5	2	3
Se	—	nd	—	—	—	—
Sm	24	2.8	Working	0.1	2.7	2.9
Sn	26	1.8	Working	0.2	1.6	2.0
Sr	44	515	Working	21	495	536
Ta	29	1.0	Working	0.1	0.8	1.1
Te	—	nd	—	—	—	—
Tb	27	0.2	Working	0.0	0.2	0.2
Th	27	17.4	Working	0.8	16.7	18.2
Tl	—	nd	—	—	—	—
Tm	—	nd	—	—	—	—
U	22	4.2	Working	0.2	4.0	4.3
V	29	14.6	Working	0.9	13.6	15.5
W	—	nd	—	—	—	—
Y	42	4.5	Working	0.4	4.1	4.9
Yb	25	0.5	Working	0.0	0.4	0.5
Zn	26	41	Working	3	38	44
Zr	39	190	Working	4	186	194

NOTES: nd: Not determined
n: Number of samples
LOI: Loss on ignition

The effect of mill head composition on analyte concentration in the Bunbury Basalt

With increasingly sophisticated analytical methods becoming routinely available from both government, university, and commercial laboratories, it is necessary to understand to what degree the processes used in sample preparation can affect the analytical result. Contamination can result from inadequate cleaning of crushing and milling equipment between samples, cross-contamination of samples through careless sample handling or numbering, and the use of reagents with unacceptably high contents of analytes of interest. A possible source of contamination, but one that is not so easy to gauge, is contamination introduced from the mill head during sample pulverization. The level of such contamination is determined by the nature of the mill head (which includes its composition and inclination to wear), the abrasiveness of the material being milled, and the milling time.

Commonly used mill head types are either metal-based (e.g. low-Cr steel, carbon steel, tungsten carbide) or silicate or ceramic (e.g. zirconia, aluminium nitride, agate). The most common mill head types found in both commercial, university, and government laboratories are tungsten carbide and low-Cr steel, although zirconia mills are available at several commercial laboratories; agate mill heads are uncommon because of their cost, and the requirement that they are operated at a lower vibration rate (hence requiring a separate mill). Apart from lithogeochemistry, assessing the extent of mill head contamination is important for isotopic analysis. For example, sample preparation with a tungsten-carbide mill head is unsuitable for Lu/Hf isotopic work, due to the ^{182}W interference on ^{182}Hf (Evins, P, 2007, written comm.).

Cruikshank and Pyke (1993) assessed the possible contamination of different mill heads by analysis of granular quartz sand, which had been milled for different times in agate, tungsten-carbide, and chrome-steel mill heads. They analysed 42 analytes by XRF and instrumental neutron activation analysis (INAA). For all three mill head types, they detected no contamination for 24 of the 42 analytes regardless of milling time, but their study involved analysis of elements with relatively high detection levels for elements of interest, such as Hf (3 ppm), Ta (3 ppm), Nb (2 ppm), La (3 ppm), and Ce (3 ppm). For the remaining elements, of the three mill head types the agate mill head introduced the fewest contaminants, but Cruikshank and Pyke (1993) noted that this had to be balanced against a high wear rate, fragility, and necessity to mill the sample for longer periods. Agate mill heads are also significantly more expensive than other materials, and require special mills to operate at a lower speed.

For the Cruikshank and Pyke (1993) study dealing with the tungsten-carbide mill head, significant contamination was noted for Co (up to 220 ppm) and W (up to 1770 ppm), with Ta contamination up to 7 ppm. Major contaminants

introduced by the chrome-steel mill head included Cr (up to 790 ppm), Fe_2O_3 (up to 0.76 %), with minor Cu, Mn, Mo, Nb, Ni, V and W. In addition to milling quartz sand, Cruikshank and Pyke (1993) also milled 15 rock samples ranging in composition from a gabbro (46.8% SiO_2) to a granite (77.2% SiO_2) in the chrome-steel and tungsten-carbide mill heads. They noted that the levels of contamination were lower for all elements compared to values for the quartz sand, and that the amount of W introduced was proportional to the SiO_2 content of the sample, suggesting a relationship between introduced contamination and abrasiveness.

E Webber, J Pyke, and B Pappas (2006, written comm.) carried out a similar type of test at Geoscience Australia for tungsten carbide, chrome steel, carbon steel, partially stabilized zirconia (PSZ), and Syalon (alloy of silicon nitride and aluminium) mill heads. They analysed for 13 elements, and found that the:

- tungsten-carbide mill head caused significant Co (113–157 ppm) and W (900–1276 ppm) contamination;
- chrome steel introduced Fe (2300–2500 ppm), Cr (508–546 ppm), Ni, Cu, and Mo (<5 ppm);
- carbon steel introduced Fe (2520–3380 ppm), Cr, Cu, and Ni (<5 ppm);
- PSZ contributed Zr (303–433 ppm), Hf (6–9 ppm), Sr (1 ppm), and Ba (2 ppm);
- Syalon introduced Al (1100 ppm) and Y (1–2 ppm).

In general, the amount of contamination increased with increased milling time. Although offering higher quality analyses in terms of detection levels than Cruikshank and Pyke's (1993) study, they did not examine the milling of rocks, and provided data for a limited range of elements.

The milling of quartz, as discussed above, is the extreme case for detecting mill head contamination, in that the harder the material being milled, the more abrasive the effect on the mill head. Another contributing factor is the durability of the mill, with mill head types such as Syalon and agate being more susceptible to wear, hence contributing more in terms of contamination. Although undocumented, it is possible that these less resistant materials may also be more prone to retain materials from previous samples, introducing another source of contamination.

In order to test for possible contamination from mill heads typically used by GSWA, about 20 kg of 10 mm chips of the Bunbury Basalt (termed BB2 here) were collected from Hanson Construction Materials Pty Ltd's Gelorup Quarry (Fig. 2), milled in either tungsten carbide, low-Cr steel, or zirconia, and subsequently analysed. The 10 mm material was crushed to a nominal particle size of 3 mm in a modified Nugget jaw crusher at GSWA's Carlisle Laboratory, and the resulting materials thoroughly washed (to remove any dusty residue) and dried. Approximately 2 kg aliquots were then milled in 200 g-capacity tungsten-carbide (150 seconds) and 100 g-capacity low-Cr steel (150 seconds) mill heads at GSWA's Carlisle Laboratory, and in a zirconia mill head in 50 g aliquots for three minutes at UltraTrace Laboratories (Canning Vale, Perth). The resulting pulps were analysed in triplicate in one batch at UltraTrace Laboratories according to the conditions summarized in Table 12. These data allow a comparison

Table 12. Analytical results for the Bunbury Basalt (BB2) milled in three different mill heads (tungsten carbide, low-Cr steel, zirconia)

Laboratory	DL	Zirconia			Tungsten carbide			Low-Cr steel			
		186082 1	186082 2	186082 3	Average	SD	186083 1	186083 2	186083 3	Average	SD
Parts per million (unless otherwise indicated)											
Au (ppb)	1	-1	-1	-1	-1	0	-1	-1	-1	-1	0
FA-ICP-MS	1	-1	-1	-1	-1	0	-1	-1	-1	-1	-1
Pt (ppb)	1	-1	-1	-1	-1	0	-1	-1	-1	-1	0
FA-ICP-MS	1	-1	-1	-1	-1	0	-1	-1	-1	-1	0
Ag	0.5	-0.5	-0.5	-0.5	-0.5	0	-0.5	-0.5	-0.5	-0.5	0
4A-ICP-MS	1	-1	-1	-1	-1	0	-1	-1	-1	-1	0
As	1	-1	-1	-1	-1	0	-1	-1	-1	-1	0
4A-ICP-MS	1	95	93	95	94	-1	93	92	91	90	-1
Ba	1	0.6	0.7	0.6	0.6	-0.1	0.6	0.7	0.6	0.6	-0.1
4A-ICP-MS	0.1	-0.1	-0.1	-0.1	-0.1	-	-0.1	-0.1	-0.1	-0.1	0.0
Be	0.1	-0.1	-0.1	-0.1	-0.1	-	-0.1	-0.1	-0.1	-0.1	0.0
Bi	0.5	-0.5	-0.5	-0.5	-0.5	0	-0.5	-0.5	-0.5	-0.5	0
Cd	0.5	-0.5	-0.5	-0.5	-0.5	0	-0.5	-0.5	-0.5	-0.5	0
4A-ICP-MS	0.1	27.1	26.5	27.0	26.9	-0.3	25.9	25.1	25.3	25.4	-0.4
Ce	0.1	27.1	26.5	27.0	26.9	-0.3	25.9	25.1	25.3	25.4	-0.4
4A-ICP-OES1	37	38	36	37	-1	52	50	49	50	36	36
4A-ICP-OES1	140	140	140	140	0	155	145	140	147	150	150
Cr	0.1	0.4	0.4	0.4	0.4	0.0	0.3	0.4	0.4	0.4	0.0
CS	0.1	0.4	0.4	0.4	0.4	0.0	0.3	0.4	0.4	0.4	0.0
4A-ICP-OES5	63	60	61	61	-2	64	61	61	62	61	63
Cu	0.05	7.30	7.20	7.30	7.30	-0.06	7.10	7.10	7.10	6.70	7.10
Dy	0.05	7.30	7.20	7.30	7.30	-0.06	7.10	7.10	7.10	6.70	7.10
4A-ICP-MS	0.05	4.10	4.00	4.00	4.00	-0.06	3.90	3.80	3.90	3.75	3.90
Er	0.05	4.10	4.00	4.00	4.00	-0.06	3.90	3.80	3.90	3.75	3.90
Eu	0.05	1.90	1.85	1.95	1.90	-0.05	1.90	1.85	1.88	1.80	-0.03
4A-ICP-MS	0.2	21.8	21.2	22.0	21.7	-0.4	21.2	20.8	20.6	20.9	-0.3
Ga	0.2	21.8	21.2	22.0	21.7	-0.4	21.2	20.8	20.6	20.9	-0.3
4A-ICP-MS	0.2	7.2	7.0	7.2	7.1	-0.1	7.0	6.8	6.9	6.6	-0.1
Gd	0.2	7.2	7.0	7.2	7.1	-0.1	7.0	6.8	6.9	6.6	-0.1
4A-ICP-OES20	-20	-20	-20	-20	0	-20	-20	-20	-20	-20	0
Ge	0.2	4.6	4.6	4.8	4.7	-0.1	4.0	4.0	4.2	3.8	-0.1
Hf	0.2	4.6	4.6	4.8	4.7	-0.1	4.0	4.0	4.2	3.8	-0.1
4A-ICP-MS	0.02	1.48	1.46	1.50	1.48	-0.02	1.44	1.44	1.44	1.42	1.44
Ho	0.02	1.48	1.46	1.50	1.48	-0.02	1.44	1.44	1.44	1.42	1.44
4A-ICP-MS	0.02	0.10	0.10	0.08	0.09	-0.01	0.12	0.10	0.10	0.08	0.10
In	0.02	0.10	0.10	0.08	0.09	-0.01	0.12	0.10	0.10	0.08	0.10
4A-ICP-MS	0.1	10.9	10.4	10.7	10.7	-0.3	10.4	10.2	10.3	9.8	10.1
La	0.1	10.9	10.4	10.7	10.7	-0.3	10.4	10.2	10.3	9.8	10.1
Li	0.5	8.5	8.0	8.5	8.3	-0.3	8.0	8.0	8.0	7.5	8.0
4A-ICP-MS	0.5	8.5	8.0	8.5	8.3	-0.3	8.0	8.0	8.0	7.5	8.0
Lu	0.02	0.50	0.48	0.50	0.49	-0.01	0.48	0.48	0.46	0.46	-0.01
4A-ICP-MS	0.02	0.50	0.48	0.50	0.49	-0.01	0.48	0.48	0.46	0.46	-0.01
Mo	0.5	1.0	1.0	1.0	1.0	0.0	1.0	1.0	1.0	1.5	1.3
4A-ICP-MS	0.5	1.0	1.0	1.0	1.0	0.0	1.0	1.0	1.0	1.5	1.3
Nb	0.5	7.0	6.5	7.0	6.8	-0.3	6.5	6.5	7.0	6.5	-0.3
4A-ICP-MS	0.5	7.0	6.5	7.0	6.8	-0.3	6.5	6.5	7.0	6.5	-0.3
Nd	0.05	17.80	17.40	17.60	17.60	-0.20	16.90	16.90	16.70	16.40	-0.12
4A-ICP-MS	0.05	17.80	17.40	17.60	17.60	-0.20	16.90	16.90	16.70	16.40	-0.12
4A-ICP-OES5	38	37	37	37	-1	38	37	37	37	42	39
Ni	38	37	37	37	-1	38	37	37	37	42	39
4A-ICP-MS	1	4	5	4	4	-1	3	3	4	3	-1
Pb	1	4	5	4	4	-1	3	3	4	3	-1
4A-ICP-MS	0.02	3.76	3.66	3.72	3.71	-0.05	3.60	3.58	3.64	3.46	-0.03
Pr	0.02	3.76	3.66	3.72	3.71	-0.05	3.60	3.58	3.64	3.46	-0.03
4A-ICP-MS	0.02	3.76	3.66	3.72	3.71	-0.05	3.60	3.58	3.64	3.46	-0.03
Rb	0.2	9.80	9.40	9.60	9.60	-0.20	9.60	9.40	9.20	9.00	-0.20
4A-ICP-MS	0.2	9.80	9.40	9.60	9.60	-0.20	9.60	9.40	9.20	9.00	-0.20
Sb	0.1	-0.2	-0.2	-0.2	-0.2	0.0	-0.2	-0.2	-0.2	-0.2	0.0
4A-ICP-OES5	34	33	34	34	-1	34	33	33	33	32	32
Sc	34	33	34	34	-1	34	33	33	33	32	32
4A-ICP-MS	0.05	5.55	5.50	5.70	5.58	-0.10	5.50	5.50	5.40	5.10	-0.06
4A-ICP-MS	0.05	5.55	5.50	5.70	5.58	-0.10	5.50	5.50	5.40	5.10	-0.06
Sn	1	1	1	2	1	0	2	2	2	2	0
4A-ICP-MS	1	1	1	2	1	0	2	2	2	2	0
Sr	1	235	228	236	233	-4	225	221	223	215	-2
4A-ICP-MS	1	235	228	236	233	-4	225	221	223	215	-2
Ta	0.1	0.4	0.4	0.5	0.4	-0.1	0.4	0.4	0.4	0.3	0.0
4A-ICP-MS	0.1	0.4	0.4	0.5	0.4	-0.1	0.4	0.4	0.4	0.3	0.0
Tb	0.05	1.20	1.18	1.22	1.20	-0.02	1.18	1.18	1.16	1.14	-0.01
4A-ICP-MS	0.05	1.20	1.18	1.22	1.20	-0.02	1.18	1.18	1.16	1.14	-0.01
Th	0.1	1.6	1.4	1.5	1.5	-0.1	1.3	1.4	1.4	1.3	-0.1
4A-ICP-MS	0.1	1.6	1.4	1.5	1.5	-0.1	1.3	1.4	1.4	1.3	-0.1
Tl	0.1	-0.1	-0.1	-0.1	-0.1	0.0	-0.1	-0.1	-0.1	-0.1	0.0
4A-ICP-MS	0.1	-0.1	-0.1	-0.1	-0.1	0.0	-0.1	-0.1	-0.1	-0.1	0.0
Tm	0.02	0.54	0.54	0.56	0.55	-0.01	0.52	0.54	0.54	0.50	-0.01
4A-ICP-MS	0.02	0.54	0.54	0.56	0.55	-0.01	0.52	0.54	0.54	0.50	-0.01
U	0.1	0.3	0.2	0.2	0.2	-0.1	0.2	0.2	0.2	0.2	0.0
4A-ICP-MS	0.1	0.3	0.2	0.2	0.2	-0.1	0.2	0.2	0.2	0.2	0.0
V	274	268	280	274	-6	282	274	272	276	268	268
4A-ICP-OES10	274	268	280	274	-6	282	274	272	276	268	268
W	0.5	-0.5	-0.5	-0.5	-0.5	0.0	91.0	86.0	85.5	-0.5	-0.5
4A-ICP-MS	0.5	-0.5	-0.5	-0.5	-0.5	0.0	91.0	86.0	85.5	-0.5	-0.5
X	0.1	38.7	36.7	38.4	37.9	-1.1	39.6	36.6	35.9	36.0	-0.4
4A-ICP-MS	0.1	38.7	36.7	38.4	37.9	-1.1	39.6	36.6	35.9	36.0	-0.4
Yb	0.05	3.40	3.30	3.35	3.35	-0.05	3.35	3.20	3.25	3.15	-0.08
4A-ICP-MS	0.05	3.40	3.30	3.35	3.35	-0.05	3.35	3.20	3.25	3.15	-0.08
Zn	1	114	113	115	114	-1	115	112	109	110	-1
4A-ICP-MS	1	114	113	115	114	-1	115	112	109	110	-1
Zr	1	231	214	225	223	-9	195	200	196	191	-1
4A-ICP-MS	1	231	214	225	223	-9	195	200	196	191	-1

NOTES: Analyses carried out at UltraTrace Laboratories

DL: Detection limit

SD: Standard deviation

between the levels of contamination between different mill head types.

Analytical results (Table 12) show that for Au, Pd, Pt, As, Bi, Cs, Ge, In, Sb, and Tl, concentrations are too low to assess any affect of the mill head on composition. For a range of elements a graphical comparison of data is shown in terms of a spider diagram (Fig. 9), where average data for the zirconia and tungsten-carbide mill heads are normalized to data for low-Cr steel; data for W are omitted because the concentration from milling in low-Cr steel was less than 0.5 ppm. For all analytes prepared in all three mill heads the low SD values for all analytes indicates acceptable precision. A comparison of mean values according to mill head type shows that Ba, Ce, Dy, Er, Ga, Gd, Hf, Ho, La, Li, Nb, Nd, Pb, Pr, Rb, Sc, Sm, Sr, Th, Y, Yb, Zn, and Zr are all higher for the zirconia mill head, although for most of these elements the difference in mean values is less than 1 ppm. Predictably, there is a significant difference in Zr (zirconia mill head average is 223 ppm, compared to 197 ppm for tungsten carbide and 190 ppm for low-Cr steel). The average values for Cr (152 ppm) and Ni (42 ppm) are higher in the low-Cr steel mill head than those for either zirconia (140 and 37 ppm) or tungsten-carbide mill heads (147 and 37 ppm). The average Co, Cu, Sn, V, and W are higher in the tungsten-

carbide milled samples compared to the other two mills, the notable differences being Co and W. Elements such as Hf, Ta, and Nb are critical for evaluating the petrogenesis of igneous rocks, where they are commonly at levels close to or less than 1 ppm. Data generated for mill head testing (Table 12) show that Hf and Nb are higher in the zirconia mill head (4.7 and 6.8 ppm respectively), but values for tungsten carbide (4.1 and 6.7 ppm) and low-Cr steel (3.9 and 6.0 ppm) are similar. Mean Ta values are indistinguishable at the level of analysis (0.3–0.4 ppm). These mill-head test results show that milling in a zirconia mill head can introduce measurable amounts of some REE and light field-strength elements (LFSE) such as Ba, Rb, Sr, and Li, as well as Th and (especially) Zr. In contrast, there are few elements introduced by either the low-Cr steel (only Cr and Ni) or tungsten-carbide (Co and W) mill heads. The lower contamination introduced by mill heads compared to the results of the tests carried out by Cruikshank and Pyke (1993) and E Webber, J Pyke, and B Pappas (2006, written comm.) can be attributed to the basalt being less abrasive than the quartz sand. Results presented here are consistent with those generated by Cruikshank and Pyke (1993) for rocks with a range of SiO₂ contents.

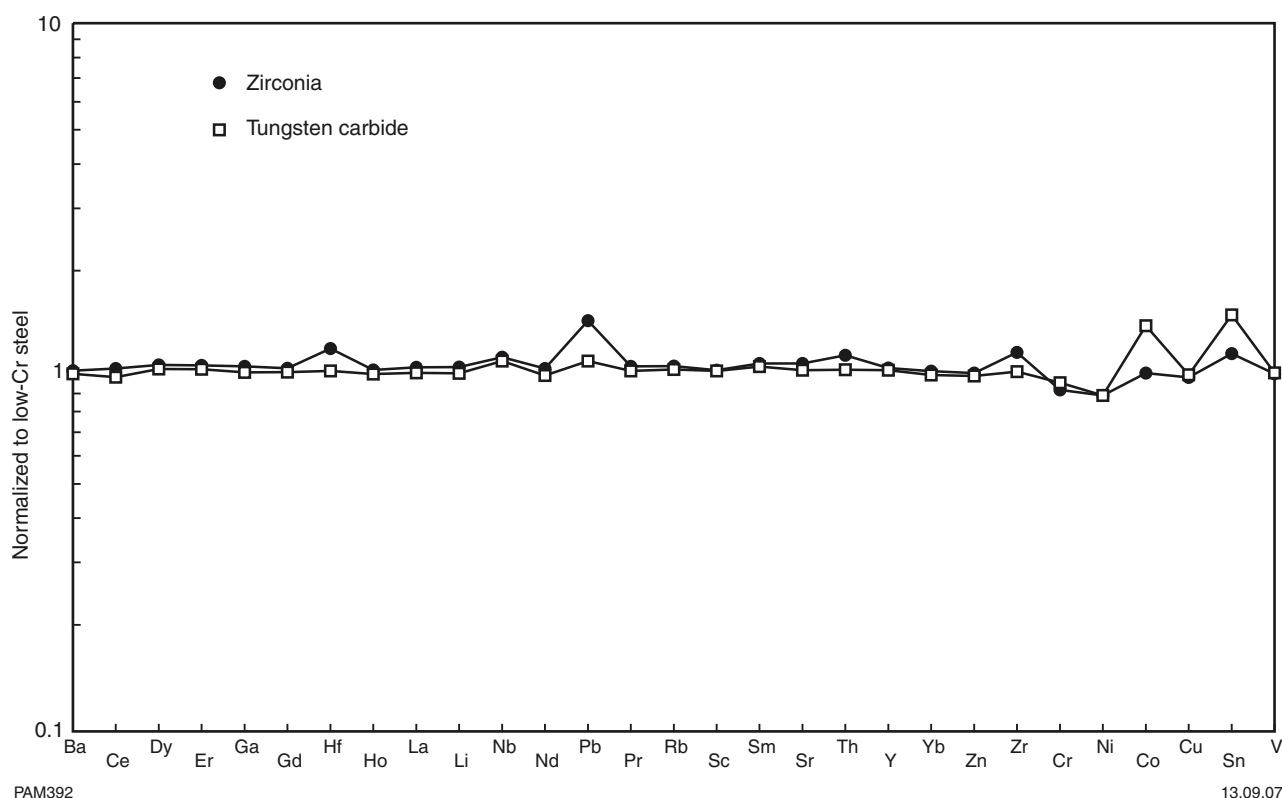


Figure 9. Spider diagram showing the concentration of selected elements in the Bunbury Basalt (BB2) milled in tungsten carbide and zirconia, normalized to concentration of elements milled in low-Cr steel. Data for W omitted as concentration is less than 0.5 ppm following milling in low-Cr steel

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