Online Supplementary Material

Analytical Methods

Petrogenesis of Fe-Ti-V oxide mineralisation in the Kalka intrusion (Giles Intrusions – Musgrave Province, South Australia)

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The samples used in this study were derived from the historical collections which are housed at the University of Adelaide. Samples of Kalka were collected by Alan T. Goode during his PhD in 1970. The coordinates of samples were determined by orthophoto by J.C. Gum.

Samples of the Kalka Intrusion were prepared as polished thin sections and polished rock chips mounted in epoxy resin. Detailed studies of sample petrography, mineralogy and inclusions were performed using an optical transmitted light and reflected light microscope, and a Hitachi SU7000 ultra-high-resolution field emission scanning electron microscope (FE-SEM). A beam accelerating voltage of 15 kV was used to produce high-resolution backscattered electron (BSE) images of rock textures and minerals and energy-dispersive X-ray spectroscopy (EDS) semi-quantitative analyses and X-ray element maps of minerals.

Whole-rock X-ray Fluorescence Spectrometry (XRF)

Whole-rock powders were powdered using an agate mortar at the University of Adelaide. Analyses were carried out at Bureau Veritas Minerals Pty Ltd (Adelaide). Samples were cast using a 12:22 flux to form a glass bead. Al_2O_3, As, Ba, CaO, Cl, Co, Cr, Cu, Fe, K_2O, MgO, MnO, Na_2O, Ni, P, Pb, S, SiO_2, Sn, Sr, TiO_2, V, Zn and Zr were determined by X-Ray Fluorescence Spectrometry. The loss on ignition (LOI) was determined using Thermo-Gravimetric Analysers. Results are reported on a dry sample basis. Standards are reported in Supplementary Table S12.

Dissolution of samples for ICPMS (University of Adelaide)

Samples were prepared by weighing 200mg of powder into acid-cleaned PFA beakers. Two rounds of digestion using a mix of 4ml 28M HF and 2ml 7M HNO_3. Samples were digested for 48 hours in acid capped on hotplate at 130°C, then dried, then redissolved for another 48 hours, then dried again. An additional few mls of HNO_3 added to each sample as it dried down. 6ml of 6M HCl was added to each sample and left capped on hotplate at 130°C for minimum 24 hours to redissolve. Samples were then aliquoted and diluted down for ICP-MS, all weights were recorded (6dp) to accurately calculate dilution factors. Ultrapure water came from a Milli-Q IQ 7000 Ultrapure water system and all acids are distilled in-house using PFA sub-boiling stills.

Whole-rock ICP-MS trace elements (University of Adelaide)

Sample solutions were analysed at Adelaide Microscopy, Adelaide University, with an Agilent 8900x ICP-MS/MS. The plasma conditions were: RF power 1550W, sample depth 10 mm and Ar carrier gas flow rate 0.95 L/min and Ar make up gas 0.1 L/min, with a Micro Mist nebuliser and Scott Type spray chamber. The collision cell was run in He mode (4 mL/min He gas flow) for ^{7}Li, ^{23}Na, ^{24}Mg, ^{27}Al, ^{29}Si, ^{43}Ca, ^{45}Sc, ^{47}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{178}Hf, ^{181}Ta, ^{208}Pb, ^{232}Th, ^{238}U where the MO^{+} reaction products measured for each element (e.g. ^{43}Ca → ^{43}Ca^{16}O measured at mass 59). On-line addition of Indium was used as the internal standard element. A series of mixed element calibration solutions 1, 10, 20, 50, 100, 200 and 500 ppb were used for quantification, made from a 10 ppm certified mixed element stock solutions from High Purity Standards (USA). All calibration solution and samples were diluted with 2% v/v HNO_3 and 18Ω water (MilliQ). The sample introduction system was rinsed in two stages with 5% and 2% HNO_3 between each analysis. Standards are reported in Online Supplementary Table S13.

Electron Microprobe (EMP) - University of Adelaide

Quantitative compositions of silicates (olivine, orthopyroxene, clinopyroxene, plagioclase, amphibole) and oxides (spinel, ilmenite) were determined using a Cameca SX-Five electron probe microanalyzer (EPMA), equipped with 5 tunable wavelength-dispersive spectrometers. The instrument is running PeakSite v6.2 software for microscope operation, and Probe for EPMA software (distributed by Probe Software Inc.) for all data acquisition and processing. Analyses were performed using operating conditions of 15 kV/20nA with a defocused beam of 5µm.

The full list of elements analysed along with primary and interference standards are presented in Tables 1 & 2. Oxygen was calculated by stoichiometry, assuming that all Fe was Fe^{2+}. Matrix corrections of Armstrong-Love/Scott φ(ρz) (Armstrong (1988)) and Henke MACs were used for data reduction. Calibration standards were NMNH-113312-44 Olivine for Mg, NMNH-135602 Corundum for Al, Wollastonite for Si and Ca, Orthoclase OR-1A for K, Albite for Na, Synthetic TiO_2 for Ti,

Vanadium for V, Cr_2O_3 for Cr, Rhodonite for Mn, Specularite for Fe, Nickel Olivine for Ni and Astimex Willemite for Zn. Detection limits (99% confidence) were <0.01 wt.% for Si, Ti, Ca, K, Mg, Al, <0.02 wt.% for Na, Fe, Cr, Ni and V, <0.03 wt.% for Ni and <0.04 wt.% for Zn.

Table 1; EPMA setup for analysis of silicates

Element and Line	Diffracting Crystal (Sp#)	Background type/fit	kV/nA/spot size(µm)	Peak Count Time	Bkgd Count Times		# bkgd points acquired (Lo/Hi)	Standards*		Overlapping element and order
					Lo	Hi		Primary Standard	Interference Standards	
Ca Ka	LPET (1)	MAN	15/20/5	20	-	-	MAN	558		
K Ka	LPET (1)	MAN	15/20/5	20	-	-	MAN	1344		
Ti Ka	LPET (1)	MAN	15/20/5	20			MAN	1342		
Na Ka	TAP (2)	MAN	15/20/5	20	-	-	MAN	735		
Si Ka	TAP (2)	MAN	15/20/5	20	-	-	MAN	558		
Fe Ka	LLIF (3)	MAN	15/20/5	20	-	-	MAN	578		
Ni Ka	LLIF (3)	MAN	15/20/5	20	-	-	MAN	1347		
V Ka	LLIF (3)	MAN	15/20/5	20			MAN	608	1342	Ti Kb (I)
Mg Ka	TAP (4)	MAN	15/20/5	20	-	-	MAN	1335		
Al Ka	TAP (4)	MAN	15/20/5	20	-	-	MAN	1325		
Mn Ka	LLIF (5)	MAN	15/20/5	20	-	-	MAN	557	577	Cr Kb (I)
Cr Ka	LLIF (5)	MAN	15/20/5	20	-	-	MAN	577	608	V Kb (I)
Zn Ka	LLIF (5)	MAN	15/20/5	20			MAN	546		

* Standard # refers to internal database.

Table 2; Standard information

Reference #	Mineral composition	Natural/Synthetic	Manufacturer
546	Willemite	Natural	Astimex
557	Rhodonite	Natural	Astimex
558	Wollastonite	Natural	P&H and Associates
577	Cr_2O_3	Synthetic	P&H and Associates
578	Specularite	Synthetic	P&H and Associates
608	Vanadium	Synthetic	Astimex
735	Albite (Amelia)	Natural	C.M. Taylor
1325	Corundum	Synthetic	NMNH
1335	Olivine	Natural	NMNH
1342	TiO_2	Synthetic	In-house
1344	Orthoclase OR-1	Natural	USGS
1347	Nickel Olivine	Synthetic	USGS

Beam damage and alkali element migration in silicate analyses were minimized via use of a defocused electron beam, in addition to use of the Mean Atomic Number (MAN) background correction (e.g. Donovan and Tingle, 1996) over traditional 2 point background interpolation. This allows single point analysis time to be greatly shortened, reducing the aforementioned effects of beam damage and element migration and their subsequent impact on the quality of analysis.

Laser Ablation (LA) ICP-MS trace elements (University of Adelaide)

Major and trace element compositions of magnetite and ilmenite were determined by LA-ICPMS at Adelaide Microscopy (University of Adelaide) using a RESOlution 193nm laser ablation coupled to an Agilent 8900x ICPMS. Analyses were conducted using a spot size of 30 μm at a laser energy of 8mJ and repetition rate of 5 Hz. A 33 s background, followed by a 36 s ablation was applied for each analysis. Samples were pre-ablated by firing 5 laser pulses onto the sample during the washout period. The primary calibration of trace elements was done using GSD-1G, using GeoReM preferred values. The measured isotopes were: ^{24}Mg, ^{27}Al, ^{29}Si, ^{43}Ca, ^{45}Sc, ^{47}Ti, ^{49}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{69}Ga, ^{72}Ge, ^{73}Ge, ^{74}Ge, ^{75}As, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{95}Mo, ^{118}Sn, ^{121}Sb, ^{133}Cs, 137Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{178}Hf, ^{181}Ta, ^{182}W, ^{202}Hg, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{232}Th and ^{238}U. Data reduction was undertaken using the program LADR (https://norsci.com/?p=ladr). For each sample, LA-ICP-MS element totals were scaled to match the average oxide totals determined independently by EMPA (see above), ensuring consistency between datasets. Standards analysed during this session are reported in Online Supplementary Table S11.

Stokes Law

Parameters used to calculate magnetite and ilmenite settling velocity:

$$v_t = \frac{2}{9}\frac{(\rho_{crystal} - \rho_{magma})gr^2}{\eta}$$

v_t = settling velocity

Magnetite: ρ = 5200 kg/m^3 and radius (r) of 0.5mm

Ilmenite: ρ = 4700 kg/m^3 and radius (r) of 0.25mm

η = Viscosity of fluid (basaltic magma estimated at ~10^4 Pa·s)

ρ = ~2700 kg/m^3 estimated for a basaltic magma

g = gravitational acceleration (9.81 m/s^2)

References

Armstrong JT (1988). Quantitative analysis of silicate and oxide minerals: Comparison of Monte Carlo, ZAF, and φ(ρz) procedures. Microbeam Analysis, D.E. Newbury, ed., San Fransisco Press, 239-246.

Donovan JJ, Tingle TN (1996). An Improved Mean Atomic Number Background Correction for Quantitative Microanalysis. Microscopy and Microanalysis, 1, pp. 1-7. https://doi.org/10.1017/S1431927696210013.