

Item DR1: Analytical Methods

Whole-rock major and trace elements for 7 samples were analysed by Central Analytical Facilities in Stellenbosch University (South Africa). Major elements were determined by X-ray fluorescence analyses (XRF) on compressed powder pellets by PANalytical Axios spectrometer with Rh tube. Precision and accuracy were better than 4% for all major elements, based on analyses of the geological reference materials NIM-G, NIM-S, BE-N, JB-1, SY-2, SY-3, BHVO-1, ARF D34 and JG1. Inductively coupled plasma mass spectrometry (ICP-MS) with four acid digests was used for the determination of whole-rock trace elements. The certified reference materials BCR-2 and BHVO-2G were used to monitor the quality control of analyses. For all elements the standard deviations were less than 15%.

Whole-rock major and trace elements for 11 samples were analysed by Genalysis Intertek Laboratory Services in Australia. Major elements were determined by X-ray fluorescence analyses (XRF) of compressed powder pellets. Calibrations used the international rock standard SARM8 as well as in-house controls. Agreement with recommended values was better than 0.6% for Cr₂O₃, Fe₂O₃, MgO, Al₂O₃ and better than for 10% for all other major elements. Trace elements were determined by inductively-coupled plasma mass spectrometry and atomic emission spectrometry (ICP-MS/ICP-AES). Every ICP-MS analysis was accompanied by control standards GTS-2a, AMIS0167, and AMIS0013 and selected samples were re-analyzed to check anomalous results. For all elements the standard deviations were less than 10%.

Both EDS and LA-ICPMS analyses of minerals were carried out in University of Tasmania, Australia at the Central Science Laboratory and ARC Centre of Excellence in Ore Deposits, respectively. About 910 analyses of plagioclase across the Koffiefontein sill were carried out on polished sections using energy dispersive X-ray spectrometry (EDS) on a FEI Quanta 600 scanning electron microscope (SEM) equipped with a tungsten filament and an EDAX Genesis Sapphire SUTW Si(Li) EDS system. We use an accelerating voltage of 20 kV. Chemical compositions displayed with ED spectra have been obtained by standardless quantification and can be considered semiquantitative only.

Major and trace elements in plagioclase (86 analyses) were determined on polished surfaces by laser-ablation inductively coupled plasma mass spectrometry (LA-ICPMS) analysis. The instrumentation involved an excimer ArF Coherent Compex Pro 110 operating at 193nm wavelength and ~20ns pulse width. The laser ablation system is an ASI (formerly Resonetics) Resolution S-155 with a large format ablation cell. The laser was coupled to Agilent 7500 quadrupole mass spectrometer. Helium flows into the laser cell at 0.35 l/min and is mixed with argon flowing at 1.05 l/min directly after ablation. The following analytical parameters and conditions were used: laser beam diameter of 80 µm, laser beam fluence ~ 3.5 J/cm², laser pulse rate 10 Hz. n. Instrument calibration was carried out ablating the NIST612 glass standard. Data reduction was undertaken by standard methods (Longerich et al., 1996) using the NIST612 glass as a primary reference material (Jochum et al., 2011). USGS glasses BCR-2g and GSD-1g were analysed as secondary standards. Reference materials were analysed two times each, consequently, every 1–1.5 h during analytical session to correct for instrumental drift. Factors contributing to precision of LA-ICPMS analyses are described in detail in Gilbert et al. (2013). In general, the precision is estimated to be better than 10% for all elements analysed in this study.

Supplementary 2 presents all whole-rock major and trace elements for the Koffiefontein sill and host shales and Supplementary 3 gives composition of plagioclase that was obtained by LA-ICPMS. A very large number of EDS analyses were generated and are not included here, but are used in Figure 1 to show the large extent of zonation of plagioclase grains. Supplementary 4 gives an explanation of the calculation procedure.

- Gilbert, S., Danyushevsky, L., Robinson, P., Wohlgemuth-Ueberwasser, C., Pearson, N., Savard, D., Norman, M. and Hanley, J., 2012. A comparative study of five reference materials and the Lombard meteorite for the determination of the platinum-group elements and gold by LA-ICP-MS. *Geostand. Geoanal. Res.* 37 (1), 51–64.
- Jochum, K.P. and 11 others, 2011. Determination of reference values for NIST SRM 610-617 glasses following ISO guidelines. *Geostand. Geoanal. Res.* 35 (4), 397-429.
- Longerich, H. P., Jackson, S. E. and Gunther, D. (1996). Laser ablation inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation. *Journal of Analytical Atomic Spectrometry* 11(9), 899-904.

Item DR2: Major and Trace Element Analyses

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Item DR3: Plagioclase Analyses

Table DR2. Plagioclase composition (ICP-MS analyses) from the rocks of Koffienfontein sill

Samples	Distance (m)	SiO ₂ wt %	Al ₂ O ₃ wt %	FeO wt %	MgO wt %	CaO wt %	Na ₂ O wt %	K ₂ O wt %	Ti ppm	V ppm	Sc ppm	Rb ppm	Sr ppm	Y ppm	Ba ppm	La ppm	Ce ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Dy ppm	Er ppm	An at%
KFN-1127-3	1.3	50.52	31.34	0.47	0.19	12.54	4.55	0.31	372	9.05	0.52	0.80	340	0.39	92	1.05	1.97	0.90	0.15	1.02	0.14	0.10	0.03	75.30
KFN-1127-3	1.3	50.11	31.76	0.26	0.26	13.13	4.17	0.23	289	8.13	0.52	0.42	339	0.19	74	0.85	1.54	0.55	0.11	0.92	0.07	0.05	0.02	77.70
KFN-1127-3	1.3	50.23	31.70	0.31	0.22	12.98	4.24	0.24	316	8.51	0.40	0.58	337	0.23	78	0.90	1.58	0.71	0.11	0.95	0.07	0.05	0.02	77.17
KFN-1127-3	1.3	50.97	30.97	0.49	0.11	12.10	4.91	0.35	377	9.25	0.47	0.80	352	0.23	117	1.24	2.13	0.73	0.11	1.29	0.11	0.04	0.02	73.14
KFN-1127-3	1.3	50.31	31.65	0.27	0.26	12.90	4.24	0.29	314	8.26	0.37	2.09	345	0.21	102	0.86	1.51	0.71	0.10	0.95	0.09	0.04	0.02	77.06
KFN-1078	5.6	49.79	32.04	0.26	0.27	13.31	4.04	0.23	297	8.62	0.45	0.46	339	0.21	68	0.87	1.54	0.69	0.17	1.01	0.07	0.04	0.02	78.47
KFN-1078	5.6	49.87	31.89	0.43	0.12	13.34	4.03	0.26	288	8.31	0.38	0.37	350	0.21	77	0.98	1.70	0.73	0.11	0.97	0.07	0.05	0.02	78.54
KFN-1078	5.6	49.27	32.38	0.33	0.18	13.73	3.79	0.25	293	8.41	0.48	0.69	344	0.27	72	1.01	1.83	0.75	0.10	1.02	0.10	0.06	0.03	80.02
KFN-1078	5.6	49.29	32.39	0.35	0.15	13.60	3.90	0.24	290	8.33	0.40	0.72	350	0.25	73	0.92	1.67	0.67	0.08	1.01	0.14	0.06	0.03	79.38
KFN-1078	5.6	49.75	32.00	0.22	0.26	13.42	4.08	0.20	294	8.40	0.38	0.41	344	0.20	71	0.86	1.57	0.65	0.12	0.99	0.08	0.05	0.01	78.42
KFN-1078	5.6	48.92	32.68	0.40	0.10	13.51	4.07	0.24	309	8.60	0.45	0.50	361	0.26	91	1.19	2.14	0.82	0.12	1.24	0.09	0.08	0.01	78.60
KFN-1078	5.6	49.96	31.90	0.27	0.21	13.23	4.10	0.25	305	8.45	0.43	0.53	345	0.18	78	0.90	1.64	0.62	0.04	0.95	0.11	0.05	0.03	78.09
KFN-1078	5.6	50.00	31.79	0.38	0.17	13.13	4.18	0.27	338	8.60	0.46	0.50	343	0.23	71	0.87	1.62	0.73	0.12	1.03	0.06	0.06	0.02	77.65
KFN-1073	10.6	50.07	31.83	0.36	0.16	13.09	4.16	0.26	326	8.72	0.39	0.87	342	0.22	86	0.94	1.72	0.72	0.11	1.13	0.12	0.04	0.02	77.68
KFN-1073	10.6	49.36	32.47	0.38	0.11	13.79	3.61	0.21	250	8.35	0.48	0.54	332	0.21	68	0.88	1.62	0.61	0.05	0.99	0.09	0.05	0.03	80.87
KFN-1073	10.6	49.66	32.13	0.48	0.26	13.25	3.87	0.28	306	9.21	0.55	2.28	337	0.28	70	0.99	1.66	0.68	0.14	1.01	0.10	0.05	0.03	79.10
KFN-1073	10.6	49.60	31.80	0.51	0.54	13.26	3.88	0.34	291	9.23	0.49	6.86	334	0.19	74	0.99	1.84	0.75	0.09	0.97	0.09	0.06	0.02	79.06
KFN-1073	10.6	49.83	32.06	0.30	0.21	13.46	3.85	0.23	267	8.37	0.45	0.35	338	0.21	67	0.87	1.47	0.66	0.07	0.93	0.06	0.03	0.02	79.44
KFN-1073	10.6	49.64	32.14	0.38	0.23	13.35	3.88	0.31	287	8.86	0.57	1.67	338	0.19	68	0.91	1.56	0.68	0.11	1.06	0.06	0.04	0.02	79.19
KFN-1073	10.6	49.53	32.29	0.35	0.18	13.61	3.72	0.24	282	8.42	0.46	2.26	340	0.27	79	0.97	1.76	0.74	0.14	0.92	0.09	0.06	0.02	80.15
KFN-1073	10.6	49.67	32.13	0.40	0.11	13.55	3.80	0.26	267	8.45	0.39	1.13	349	0.22	72	0.91	1.66	0.62	0.10	1.08	0.06	0.05	0.02	79.75
KFN-1073	10.6	49.85	32.04	0.37	0.14	13.45	3.82	0.26	280	8.40	0.43	0.44	335	0.18	64	0.85	1.51	0.59	0.09	0.95	0.07	0.05	0.03	79.55
KFN-1051-8	31.8	48.59	33.19	0.31	0.09	14.00	3.50	0.25	260	9.45	0.56	1.84	341	0.42	75	1.31	2.30	1.08	0.20	1.03	0.11	0.10	0.05	81.56
KFN-1051-8	31.8	49.47	32.25	0.48	0.16	13.34	3.94	0.29	284	8.85	0.51	2.14	341	0.22	77	0.96	1.68	0.72	0.09	1.04	0.06	0.04	0.02	78.90
KFN-1051-8	31.8	49.80	32.08	0.44	0.09	13.27	4.02	0.24	288	8.27	0.51	0.33	335	0.20	65	0.87	1.60	0.71	0.09	1.00	0.08	0.06	0.01	78.50
KFN-1051-8	31.8	50.05	32.01	0.32	0.10	13.04	4.18	0.23	291	8.54	0.53	0.65	335	0.21	66	0.86	1.53	0.66	0.14	1.00	0.08	0.03	0.02	77.54
KFN-1051-8	31.8	49.84	32.15	0.32	0.15	13.34	3.90	0.23	277	8.61	0.46	0.25	337	0.18	67	0.84	1.55	0.73	0.09	0.93	0.09	0.05	0.02	79.09
KFN-1042	41.6	50.15	31.88	0.35	0.11	13.10	4.07	0.26	292	8.70	0.40	0.52	340	0.19	72	0.90	1.57	0.60	0.12	0.93	0.07	0.04	0.01	78.05
KFN-1042	41.6	49.78	32.11	0.35	0.15	13.50	3.79	0.24	269	8.03	0.47	0.37	334	0.19	64	0.88	1.55	0.60	0.12	0.96	0.11	0.05	0.01	79.73
KFN-1042	41.6	49.59	32.25	0.42	0.11	13.51	3.81	0.24	268	8.52	0.39	0.38	341	0										

KFN-926	82.6	50.59	31.36	0.47	0.10	12.67	4.44	0.29	336	9.07	0.44	0.46	346	0.21	90	0.95	1.68	0.80	0.10	1.08	0.07	0.06	0.01	75.93
KFN-903-8	104.8	50.84	31.22	0.46	0.13	12.56	4.42	0.30	347	9.08	0.51	0.45	353	0.22	96	1.02	1.77	0.69	0.13	1.17	0.07	0.04	0.02	75.87
KFN-903-8	104.8	51.31	30.89	0.46	0.08	12.00	4.80	0.37	394	8.52	0.54	0.57	377	0.24	120	1.10	2.00	0.88	0.11	1.40	0.11	0.07	0.01	73.43
KFN-903-8	104.8	51.26	30.82	0.53	0.13	11.88	4.89	0.41	438	8.59	0.46	2.32	367	0.26	134	1.24	2.16	0.89	0.10	1.29	0.11	0.05	0.03	72.87
KFN-903-8	104.8	50.54	31.38	0.51	0.08	12.78	4.34	0.30	332	8.68	0.44	0.51	353	0.19	93	0.90	1.59	0.76	0.12	1.20	0.07	0.05	0.02	76.51
KFN-903-8	104.8	50.04	31.76	0.43	0.14	13.21	4.07	0.27	319	9.10	0.45	0.41	348	0.20	85	0.89	1.65	0.70	0.13	0.99	0.09	0.05	0.01	78.22
KFN-903-8	104.8	51.15	30.87	0.47	0.11	12.27	4.72	0.32	387	8.72	0.56	0.59	348	0.21	95	1.01	1.73	0.69	0.11	1.15	0.12	0.04	0.01	74.16
KFN-903-8	104.8	50.36	31.58	0.43	0.13	12.87	4.25	0.30	325	9.15	0.45	1.25	349	0.18	87	0.92	1.61	0.69	0.08	1.04	0.10	0.05	0.02	77.00
KFN-880	128.6	51.28	30.84	0.49	0.08	12.07	4.81	0.34	407	8.45	0.52	0.64	371	0.25	113	1.22	1.99	0.79	0.10	1.27	0.10	0.03	0.01	73.51
KFN-880	128.6	52.02	30.33	0.49	0.07	11.29	5.29	0.41	503	7.65	0.48	0.68	396	0.23	155	1.43	2.42	0.98	0.16	1.59	0.11	0.07	0.01	70.22
KFN-880	128.6	52.40	29.96	0.45	0.10	11.04	5.50	0.43	518	8.36	0.55	1.04	367	0.18	164	1.39	2.38	0.90	0.13	1.19	0.06	0.04	0.02	68.92
KFN-880	128.6	52.64	29.85	0.49	0.04	10.68	5.81	0.35	551	5.85	0.46	0.95	456	0.30	333	1.96	3.08	1.17	0.20	3.26	0.12	0.06	0.02	67.01
KFN-880	128.6	51.05	31.15	0.46	0.08	12.14	4.71	0.32	399	8.70	0.55	0.61	364	0.23	108	1.15	1.96	0.79	0.18	1.27	0.12	0.05	0.02	74.02
KFN-880	128.6	51.23	30.86	0.52	0.07	12.05	4.83	0.35	420	8.76	0.49	0.58	356	0.19	104	1.14	1.86	0.81	0.11	1.16	0.10	0.03	0.01	73.39
KFN-871	136.7	52.71	29.74	0.41	0.09	10.69	5.74	0.50	638	6.58	0.40	0.74	406	0.27	206	1.73	2.95	1.20	0.17	1.90	0.11	0.06	0.02	67.30
KFN-871	136.7	52.64	29.83	0.46	0.05	10.63	5.80	0.45	630	6.33	0.38	0.85	430	0.31	251	1.93	3.15	1.22	0.20	2.59	0.10	0.08	0.04	66.92
KFN-871	136.7	53.37	29.36	0.43	0.04	9.87	6.33	0.46	577	4.27	0.37	1.03	449	0.41	339	2.61	4.51	1.66	0.28	3.00	0.13	0.07	0.03	63.28
KFN-864-5	143.2	53.03	29.42	0.48	0.06	10.03	6.27	0.57	510	3.93	0.42	1.23	501	0.25	327	2.19	3.49	1.45	0.22	3.49	0.11	0.07	0.04	63.87
KFN-864-5	143.2	53.88	28.80	0.46	0.07	9.62	6.45	0.60	527	4.07	0.45	1.11	451	0.25	298	1.95	3.16	1.15	0.18	2.34	0.15	0.06	0.02	62.25
KFN-864-5	143.2	53.57	28.77	0.48	0.05	9.68	6.61	0.71	401	2.89	0.28	4.54	506	0.37	395	2.82	4.64	1.78	0.20	3.54	0.14	0.07	0.03	61.80
KFN-864-5	143.2	54.05	28.69	0.44	0.08	9.49	6.52	0.60	576	4.44	0.41	1.12	445	0.24	308	1.92	2.91	1.07	0.11	2.18	0.11	0.05	0.02	61.68
KFN-864-5	143.2	53.23	29.31	0.47	0.07	10.11	6.15	0.52	689	6.27	0.44	1.00	427	0.27	233	1.64	2.80	1.04	0.17	1.91	0.12	0.05	0.01	64.48
KFN-864-5	143.2	53.07	29.33	0.48	0.07	9.81	6.34	0.78	568	4.62	0.32	6.25	450	0.22	294	1.90	3.12	1.22	0.20	2.29	0.09	0.05	0.02	63.08
KFN-860a	148.7	51.50	30.64	0.44	0.11	11.67	5.11	0.42	469	7.66	0.43	0.81	375	0.24	127	1.19	2.02	0.87	0.12	1.45	0.11	0.06	0.03	71.63
KFN-860a	148.7	51.59	30.65	0.39	0.14	11.66	5.10	0.37	448	7.61	0.49	0.69	380	0.23	132	1.19	2.03	0.94	0.17	1.43	0.09	0.03	0.02	71.63
KFN-860a	148.7	51.75	30.52	0.47	0.08	11.38	5.30	0.40	475	7.82	0.44	0.79	380	0.23	137	1.18	2.10	0.85	0.14	1.36	0.06	0.05	0.01	70.36
KFN-860a	148.7	52.48	29.89	0.39	0.13	10.92	5.63	0.46	542	6.97	0.41	0.77	400	0.22	175	1.42	2.35	1.01	0.11	1.61	0.07	0.05	0.02	68.21
KFN-860a	148.7	52.66	29.75	0.40	0.12	10.69	5.77	0.48	577	6.81	0.36	0.84	401	0.24	192	1.45	2.44	0.94	0.18	1.70	0.15	0.06	0.02	67.17
KFN-860a	148.7	51.91	30.31	0.39	0.15	11.43	5.30	0.40	510	7.46	0.44	0.82	390	0.25	153	1.33	2.26	0.91	0.12	1.51	0.11	0.05	0.01	70.42
KFN-860a	148.7	52.15	30.16	0.39	0.16	11.29	5.36	0.40	463	7.64	0.48	0.75	379	0.21	148	1.21	1.96	0.77	0.11	1.41	0.08	0.04	0.02	69.94
KFN-860a	148.7	51.92	30.31	0.41	0.14	11.37	5.34	0.42	464	7.77	0.41	0.75	383	0.17	147	1.15	2.02	0.76	0.09	1.42	0.09	0.04	0.02	70.19
KFN-850	158.6	51.64	30.46	0.50	0.06	11.08	5.65	0.																

Item DR4: Notes on Calculations

Relative concentrations:

We have presented relative concentrations for all incompatible elements. We have divided actual concentration in each sample by that in the average chilled margin. It is exactly the same principle used extensively for the REE. They differ markedly in their abundance in a single rock, but by normalizing to mantle or some other source material much smaller ranges in values are obtained. We use the same principle here, but normalize to the composition of the presumed parent liquid. As a result all chill compositions plot at unity, whereas the actual concentrations can range from ppb to many ppm and would be impossible to show on a single graph.

Fractionation model

Typical models of fractionation using the Rayleigh Law usually have a constant D due to constant proportion of minerals crystallizing. However, in this instance, the largest influence on the value of D is the proportion of trapped liquid, which has an effective D of unity, and for all minerals it is essentially zero for the incompatible elements. Modelling a system with a variable D is best done by dividing the process into very small increments, and for each successive increment the D value can be changed. That allows calculation of the liquid composition after each increment. It is then necessary to calculate the bulk rock composition for that stage. We illustrate this principle with an example.

Consider a liquid column 100 m thick. Initial (relative) concentration for an incompatible element is 1. We will take 5 m increments. (Note that in the more rigorous modelling in our text we use 1 m intervals, but because that represents only 1/169 of the total crystallization interval, F becomes so close to unity – 168/169 – that the change in liquid composition appears minimal in the fourth decimal place. The use of 5 m increments here shows the principle more clearly.) It is assumed that D for all minerals is zero, and D for liquid is unity. The bulk D is then controlled totally by the proportion of trapped liquid. At each increment D is decreased by 0.1 from an initial value of 0.9 (90% trapped liquid). New values for Co, F and D need to be calculated from which C_L is determined at each increment.

Step 1: Co = 1. F = 95/100 = 0.95. D = 0.9. C_L/C_O = 1.005. C_L = 1.005.

The rock that formed contained 10% of primocrysts with zero concentration of the element and 90% liquid with concentration of 1.005. (It should perhaps be 1.0025, being half-way between the composition at 0 m and 5 m, but the difference is totally trivial.) Thus the rock contains 0.1 * 0 + 0.9 * 1.005 = 0.905.

Step 2: Co = 1.005 (i.e. C_L from step 1). F = 90/95 = 0.947. D = 0.8. C_L/C_O = 1.011. C_L = 1.016.

The rock contains 0.2 * 0 + 0.8 * 1.016 = 0.81.

Step 3: Co = 1.016 (i.e. C_L from step 2). F = 85/90 = 0.944. D = 0.7. C_L/C_O = 1.012. C_L = 1.023.

The rock contains 0.3 * 0 + 0.7 * 1.023 = 0.716.

Step 4: $C_o = 1.023$ (i.e. C_L from step 3). $F = 80/85 = 0.941$. $D = 0.6$. $C_L/C_o = 1.025$. $C_L = 1.049$.

The rock contains $0.4 * 0 + 0.6 * 1.049 = 0.629$.

The concentrations in the rocks formed from the base upward have changed from unity in the chill, to 0.6 after 20 m. The actual liquid at that level has become enriched to 1.05, but the decreasing proportion of trapped liquid results in a significant decrease in the bulk rock.

Combining the roof facies into the bottom facies to give a single upward geochemical fractionation trend.

The modelling assumes fractionation of 169 m of magma in a single direction, although the actual rocks formed a thin (20 m) roof facies and 149 m of the main body. Those 20 m of roof facies have a slightly different (more evolved) composition from the floor facies. To get an estimate of the composition of the rock forming at any stage of fractionation, it is necessary to add together the composition of a rock in the floor facies with a small proportion of rock from the roof facies. We have done this calculation by taking $20/169$ the average concentration of IE in the roof facies and adding it to $149/169$ of the individual floor rock compositions. The height of each sample has then been increased by $169/149$ of its original value. Thus, the sample at the Sandwich Horizon, originally at 149 m, is now at 169 m in the fractionation profile.