DISCUSSION

The results of the Raman analysis indicate the presence of H₂O, CO₂, N₂ and CH₄ in the fluids. The Raman responses in inclusions, where microthermometry had suggested the presence of volatiles, were not as good as was expected. Microthermometry suggested that gases other than CO₂ were present in the fluids. Many inclusions formed clathrates which melted at temperatures above 0°C, and some even had clathrate melting temperatures above 10°C. Furthermore, T final melting (CO₂) in fluid inclusions containing both liquid and vapour CO₂ occurred at temperatures below -56.6°C (the temperature at which final melting in pure CO₂ fluids occurs). When some of these inclusions were analysed, the Raman responses for most gases, including CO₂, was generally poor. Thus, the evolution of the gas content of the fluids could not be accurately assessed using this method.

The information that was obtained, however, does provide some insight into the nature of the fluids. The samples from Spoedwel and Houtenbek contain fluids associated with the sulphide paragenesis, and in addition to them containing significant amounts of solutes (indicated by PIXE analysis), the presence of N₂, CO₂ and CH₄ has been detected. The fluid inclusions from Grass Valley were associated with the precipitation of hydrothermal cassiterite and small amounts of galena, sphalerite and chalcopyrite. These fluids contained $CO_2 \pm N_2 \pm CH_4$. Thus, these gases were certainly present in the fluids associated with stage 2 (i.e. the precipitation of the sulphide assemblage) in the paragenetic sequence. In addition, the methane peak position served as an external geobarometer, from which pressure estimates of the true entrapment temperature of the fluids is possible. At Spoedwel, the pressure at which the fluids in fluorite were trapped was approximately 450 bar. At Grass Valley the late stage Type 5 fluid inclusions were trapped at pressures between 110bar and 450 bar. The entrapment pressure for fluids at Spoedwel and Grass Valley are identical in samples SP6 and GV02, and are relatively low, reflecting the facture systems.

The results of the Raman analysis prompted further study of the gas chemistry of the fluid inclusions, and attempts to identify, and quantify the volatiles associated with the different stages in the paragenetic sequence were made by means of Quadrupole Mass Spectrometry.

6.3 QUADRUPOLE MASS SPECTROMETRY

Quadrupole Mass Spectrometry (QMS) of fluid inclusion gases was chosen in order to determine the gas/volatile content of fluids associated with each of the three mineral assemblages recognised in the Bushveld granites. Analytical techniques such as microthermometry and Raman spectroscopy have indicated the presence of CO_2 , N_2 and CH_4 in the fluids, but reliable quantitative data from these techniques was not obtained. In addition, several questions were raised by the fluid inclusion microthermometry which required detailed spectrometric analysis to be answered. For example,

- Clathrate melting temperatures above 10 °C cannot be accounted for by the presence of CO₂ alone. Are CH₄ and/or N₂ clathrates, which affect phase equilibria (Murphy and Roberts, 1996), responsible for these elevated final melting temperatures?
- 2) CO₂ seldom occurs unaccompanied by N₂ and/or CH₄ (van den Kerkhoff, 1990). In what proportions are these volatiles present in the fluids?
- 3) Can the fluids be categorised in terms of their volatile content?
- 4) Is it possible to determine at what stage in the evolution of the magmatic fluid that N₂ and CH₄ became significant, and can this be used to recognise the point at which the external fluid was introduced?

OVERVIEW

Quadrupole Mass Spectrometry is a destructive technique used for analysis of the volatile content of fluid inclusions. The fluid inclusion gases are released by crushing or decrepitating (heating the sample until the fluid inclusions burst) small samples under vacuum. The gases are passed through an inlet system to the ionizing filament. Most gases are "cracked" into smaller fragments at the quadrupole analyzer source, and these ionized molecules and molecular fragments are detected by a secondary electron multiplier. Determination of the relative abundances (mole fractions) of gases in a complex gas mixture requires the use of a matrix fitting procedure, provided as part of the operating software of the quadrupole (Jones and Kesler, 1992). The theory behind

into account cracking patterns (relative intensities of parent and "cracked" peaks at a particular pressure) for each gas in an analysis and delineates multiple contributions to masses by a series of simultaneous equations in a matrix. A correlation coefficient determined for each analysis defines how well the final composition fits the original raw data (Jones and Kesler, 1992)

EQUIPMENT

Analyses were carried out in the Department of Geological Sciences, University of Michigan, using a VG SXP600 quadrupole mass spectrometer (Figure 6.28). The system used in the laboratory is described by Graney and Kesler (1995), and is briefly reviewed here. The system has dual inlet ports, a closed electron source, and a secondary ectron multiplier (SEM) detector. The number of masses (1 to 16) monitored by the Quad94 software package, and the number of counts made at each mass are operator controlled.



Figure 6.28 Photograph of the Quadrupole Mass Spectrometer at the University of Michigan.



Figure 6.29 Schematic diagram of the inlet systems on the University of Michigan quadrupole mass spectrometer (re-drawn from Jones and Kesler, 1992).

SAMPLE MATERIAL

The samples chosen for crush and decreptation analyses were ones on which petrography and microthermometry had already been carried out. A list of the samples from each deposit is shown below (Table 6.7).

DEPOSIT	SAMPLE	SAMPLE DESCRIPTION
Grass Valley	MF3A	Subsolvus granite.
	GV01	Quartz vein associated with hematite. CO2 fluid inclusions
		present.
	GV02	Quartz associated with hydrothermal cassiterite.
	GV04	Massive, pegmatitic quartz associated with pyrite and chlorite.
	GV05	Quartz vein.
	GV07A	Euledral quartz crystals lining walls of open fracture
		-generation 1.

Table 6.7List of samples chosen for QMS from Grass Valley, Spoedwel, Albert,Leeufontein and Houtenbek.

DEPOSIT	SAMPLE	SAMPLE DESCRIPTION
	GV07B	Euhedral quartz crystals in open fracture
		-generation 2.
	GV08	I te stage fluorite.
Speedvel	SP4	b edium-grained hypersolvus granite with minor quartz.
	SP5	Quartz vein material with massive hematite.
	SP6	Graphic granite.
	3P9	Fine-grained granite.
	SP13	Massive sulphide ore with late stage fluorite veins.
	Li	Vein quartz associated with chalcopyrite.
Albert	RPII IIA	Vein quartz.
	RP1 11B	Vein quartz.
	RP2 20B	Fluorite containing fluid associated with sulphide and
•		hematite/fluorite assemblages.
	RP2 27A	Quartz vein associated with hematisation and chloritisation of
		the host rock.
	RP2 29	Subsolvus granite which has been mildly hematised.
	AS25 10C	massive, quartz vein material with stringers of hydrothermal
		arsenopyrite, sphalerite and chalcopyrite.
	RPI 11A	Vein quartz.
Lecufontein	BF2	Tourmaline spheroid.
	TB	Tourmaline spheroid.
	KK03	Vein quartz associated with hematite.
·	KK01	Tournaline crystals.
	BBK1	Coarse-grained Klipkloof Granite.
	WG35	Fine-grained Klipkloof Gmaite.
	NEBO	Nebo granite.
·	WG03	Albitised Klipkloof Granite.
·	WG43	Fine-grained Klipkloof Granite
	ALB	Albitised Klipkloof Granite
Houtenbek	HBF	Fluorite.

Table 6.7 continued List of samples chosen for QMS from Grass Valley, Spoedwel, Albert, Leeufontein and Houtenbek.

METHODS

Samples for the crush analyses were prepared by separating quartz and fluorite from the other minerals, using a magnetic separator and then hand picking grains to ensure purity of the sample. In most cases, material where different quartz generations could be separated by hand (e.g. quartz veins with multiple growth stages) was selected.

Samples of between 5mg and 50mg, which had been baked in an oven (at 60°C) to drive off excess surface water, were placed in a stainless steel sample holder. The sample holder was bolted to the base of the modified Nupro valve. Pressure in the sample chamber is then reduced using roughing and turbomolecular pumps until the pressure at the pump is $<10^{-7}$ torr. The sample was then crush d with the turbomolecular pump on-line (Graney and Kesler, 1995).

The samples selected for the decrepitation analyses were fragments of doubly polished thin sections which had been mapped, and on which microthemometry had already been done. Wherever possible, fragments containing only one known fluid inclusion assemblage were chosen. However, this proved to problematic, because the samples contain numerous inclusions, and on such a small scale it was difficult to be certain that no fluid inclusions from other assemblages were present. The samples was placed in quartz tubes which are connected to the inlet system with Teflon seals. The inlet system is then evacuated and the tubes are heated with a resistance furnace. The rate of heating was controlled by a Variac rheostat in line with a temperature controller connected to a thermocouple inside the furnace. The fluid inclusions burst when the internal pressure exceeds the strength of the host mineral and the gases are liberated. The masses analysed for were: 2 (H₂); 12 (C⁺); 14 (N⁺); 15 (CH₃⁺/NH⁺); 16 (O⁺/CH₄⁺/NH₂⁺); 18 (H₂O⁺); 28 (N₂/C₂H₄⁺/CO⁺); 35 (H₂S); 34 (H₂³²S⁺/³⁴S⁺); 36 (HCl); 40 (Ar⁺); 44 (CO₂⁺/N₂O⁺); 48 (SO⁺).

The spectra generated are plots of SEM current (mA) (or Intensity expressed at the negative logarithm of the SEM current) against time. In crush analyses, all the gas is liberated simultaneously and an abrupt increase in detector response occurs

milliseconds after crushing, which is observed as a sharp jump in the spectrum. With time, the response decays until all masses return to background levels. The number of cycles varied between 300 and 500 depending on how long it took for the sample to return to background.

In the decrepitation analyses, temperature was gradually increased and recorded in connection with time and number of cycles, so that the temperature of individual inclusion bursts could be determined and the amounts of each gas liberated from an inclusion could be measured.

RESULTS

The results of the crush analyses are shown in Table 6.8 The samples are tabulated according to deposit. The results have been normalised and are reported in mole %.

The fluids are predominantly aqueous, consisting of between 92 to 99 mole % water (Figure 6.30). The samples containing the lowest amount of water are those associated with the late stage precipitation of quartz-hematite veins at Spoedwel and Grass Valley, and contain considerable amounts of CO_2 (2 to 6 mole %). In addition to CO_2 , most samples contained minor amounts of N_2 CH₄, C_2H_6 , Ar, HCl, and SO₂.



Figure 6.30 Bar chart showing the percentage of water in fluid inclusions from Grass Valley, Houtenbek, Spoedwel, Albert and Leeufontein.

Filename	H2O	N2	H2S	SO2	SO2+H2S	CH4	C2H6	C3H8	CnHn	Ar	CO2	HCI	H2
GRASS V	ALLEY								}				
GV04	99.75942	0.017724	0.005622	0.001528	0.007149	0.007255	0.00213	0	0.009385	0,000408	0.13803	0.000872	0.067014
GV05a	98.87713	0.077294	0.004002	0.004917	0.008919	0.014995	0.003414	0	0.018409	0.001617	0.988661	0.00198	0.025991
GV05b	92.58427	0.322211	0.003515	0.007741	0.011256	0	0.004943	0.040011	0.044955	0,003629	6.995985	0.002687	0.03501
GV06d	98.581	0.164452	0.004351	0.009117	0.013468	0.014001	0.003218	0	0.017219	0.002363	1.174066	0.001922	0.045003
GV07A8	99,73043	0.146396	0.006028	0.0019	0.007929	0.005509	0.004794	Ó	0.010304	0.000228	0.046011	0.000602	0.058014
GV0788	99.78592	0.06678	0.002246	0.003005	0.005251	0,00823	0.002799	0	0.011029	0,000696	0.094028	0.001281	0.03501
GV08	97.88761	0.034596	0.004324	0.001353	0.005877	0.075252	0.003522	0	0.078774	0	1.795007	0.000677	0.197662
MF3A	98.90125	0.111795	0.008759	0.024008	0.032766	0.022007	0.005871	0	0.027878	0.002058	0.920291	0.003961	0
XGV01	98.73211	0.104574	0.004144	0.005992	0.010135	0.009314	0.003717	0	0.013032	0.001554	1.110147	0.002445	0.026003
XGV02	99,37996	0.120137	0.003495	0.003426	0.00692	0.009338	0.003054	0	0.012393	0,001473	D.436206	0.001895	0.041019
		[{							
ALBERT		{			1	}							······································
AS25 10c	99.16976	0.067212	0,00219	0.003371	0.005561	0.011002	0.003104	0	0.014106	0.001379	0.703126	0.001847	0.037007
AS25 10C	99.12162	0.074736	0.00361	0.006708	0.010318	0.00203	0.002387	0.009072	0.013489	0,000667	0.742162	0	0.037008
RP1 11a	99.86307	0.058732	0.003072	0.006633	0.009705	0.006408	0,002532	0	0.00894	0.001792	0.056012	0.00175	0
RP1 11b	99.88866	0.050089	0.003156	0.004605	0.00776	0.005254	0.002409	0	0.007663	0.001489	0.043008	0.00133	0
RP11 11	99.83318	0.061256	0.003155	0.001704	0.004859	0.008751	0,00257	0	0.011321	0.001142	0.043011	0.001221	0.044012
RP2 27	99.73691	1.069615	0.004489	0.008927	0.013416	U.011002	0.003815	0	0.014817	0.001822	0.116025	0.00338	0.04401
RP2 20B	99.76633	J.033105	0.003447	0.002927	0.006374	0.035026	0.002865	0	0.037891	0.000182	0.035026	0.001999	0,119089
RP2 27A	99.71825	0.073	0.012	0.011	0.023	0.015	0.004344	0	0.019344	0.003468	0.102	0,003939	0.057
RP2 29	99.73476	0,073	0.009737	0,018	0.027737	0.013	0.006564	0	0.019564	0.004114	0,136	0.004823	Q

Filename	H2O	N2	H2S	SO2	SO2+H2S	CH4	C2H6	C3H8	CnHn	Ar	CO2	HCI	H2
						L							
SPOEDWE	ΞĹ,					L				-			
L1	99.88967	0,033967	0.003043	0.000916	0.003959	0.009829	0.002195	0	0.012024	0.000764	0.059012	0.0006	0
SP13	99,8423	0.127649	0	0.003097	0.003097	0.023016	0.003936	00	0.026952	0	0	0	0
SP4	99.80551	0.052776	0	0.001435	0.001435	0	0.003335	0	0.003335	0.000902	0.136042	0	0
SP5	96,82295	0.179822	0.004503	0.00306	0.007563	0.028003	0.004262	Q	0.032265	0.001897	2.91436	0.002142	0.039005
SP6	99,6323	0.078	0.002328	0.002443	0.004771	0.019	0.002987	0	0.021987	0.001358	0.260001	0.001579	0
SP9	99.70441	0.030094	0.005906	0.00159	0,007495	0.024011	0.002184	0	0.026195	0.000227	0.113051	0.00047	0,118054
·····				{	1				1				
HOUTENE	BEK	1		· · · · · · · · · · · · · · · · · · ·	1	,,,]				
HBF	99.73708	0.021335	0.005596	0.003532	0.009128	0.030021	0.003116	0	0.033138	0	0.038063	0.001174	0.110078
		1	1						}			· · · · · · · · · · · · · · · · · · ·	*****************
LEEUFON	TEIN - EAS	ST OF MAR	BLE HALL	•		······			•			· ····	** ***********
ALB	98.8548	0.637992	D.005122	0.012	0.017122	0.028	0	0	0.028	0.019	0.438995	0.004088	Ò
BBK1	99.72005	0	0.003595	0.004205	0.007799	0.06801	Ū Ū	0	0.06801	0	0.202028	0.002108	0
BF2	99.20734	0,556201	0.002532	0.004096	0.006629	C.027016	0.003474	0	0.03049	0.007751	0.165095	0.002481	0
KK01	99.14088	0.092336	0	0.001645	0.001645	0.014002	0.002892	0	0,016895	0,001543	0.745127	0.001575	0
KK03	99.41086	0.1308	0.004295	0.003697	0.007993	0.16974	0	0	0.16974	0	0,278574	0.002033	0
ТВ	99.74531	0,072	0.002552	0.002417	0.004969	0.051	0.002842	0	0.053842	0.004883	0.119	0	0
WG03	99.74914	0.094507	0.002305	0.002914	0.005219	0	6.003701	0	0,003701	0.0044	0.142101	0.000928	Ū.
WG35	99,59523	0.160282	0.004257	0.004056	0,008313	0.022006	0	0	0.022006	0,009112	0.205054	0	0
WG43	99.13435	0.578628	0.004013	0,004661	0.008674	0.066049	0	0	0.066049	0.008456	0,201149	0.002697	0



Figure 6.31 Bar charts showing the concentrations of H_2S and SO_2 (mole %) in samples from Grass Valley (A), Houtenbek and Spoedwel (B), Albert (C) and Leeufontein (D).

At Grass Valley, the early fluids associated with cassiterite precipitation (XGV02) contain equal amounts of H_2S and SO_2 . However, fluids associated with late stage quartz veins (XGV01, GV05 and GV07) tend to contain greater amounts of SO_2 . Samples GV04 and GV07a (first vein quartz generation) which is associated with pyrite, contain greater amounts of H_2S . The fluids associated with the subsolvus granite (MF3a) contain approximately three times more SO_2 than the fluids associated with sulphide-bearing quartz veins.

The fluorite samples from Houtenbek (HBF) and Spoedwel (SP13), and the late stage hematite-quartz sample from Spoedwel (SP5), contain more SO₂ than the hematilised hypersolvus granites hosting disseminated sulphide mineralisation. The H_2S content of the fluids in all samples associated with mineralisation, except the late stage fluorite (SP13), is greater than the SO₂ content.

At Albert, the subsolvus host granites (RP2 29) contain comparable amounts of SO_2 and H_2S as the subsolvus granite at Grass Valley (MF3a). Quartz vein material with no sulphides (RP1 11a and b) contains more SO_2 than H_2S , while the opposite is true for veins containing sulphide mineralisation.

The fine-grained (WG03, WG35, WG43) and coarse-grained (BBK1) Klipkloof Granites contain similar sulphur contents. Klipkloof Altered Granite ie. touronatinised and albitised material (BF2 contains higher WG03), SO and concentrations than the unaltered rock. The fluids associated with quartz-hematite veins contain slightly more H₂S (KK03), and the fluids in tourmaline crystals (KK01) contain no H₂S.



Figure 6.32 Bar charts showing the CO₂, CH₄ and N₂ concentrations (mole %) of fluids in samples from Grass Valley (A), Houtenbek and Spoedwel (B), Albert (C) and Leeufontein (D).

The concentration of CO_2 in the fluids associated with mineralisation at Grass Valley, and with the subsolvus granites, is minor in comparison with the high concentrations in the fluids associated with hematite precipitation in quartz generations 7 and 8 in vein quartz (GV05b). These fluids are trapped as secondary trails of inclusions in fluorite (GV08). N₂ (\pm CH₄) are more abundant in the subsolvus granite (MF3a) and in the late stage fluids trapped in vein quartz (GV05a, b and d). The fluids associated with hydrothermal cassiterite and sulphide mineralisation contain small amounts of N₂ and CO₂.

The late stage quartz-bematite veins at Speedwel contain large amounts of CO_2 in comparison with the earlier fluids associated with sulphide mineralisation and which are trapped in earlier generations of quartz veins. The N_2 content of these fluids is also greater than the earlier fluids.

The concentration of N_2 is relatively uniform in the samples from Albert. The host granite (RP2 29) contains similar amounts of N_2 , CO₂ and CH₄ as the quartz veins. The late stage fluorite contains greater amounts of N₂ than the quartz veins and host granite. Sample AS25 10C contains significant amounts of CO₂.

The N₂ content of the fluids increases from the hydrothermally altered Nebo Granite (Coarse-grained Klipkloof Granite) through to the fine-grained Klipkloof Granite, and is most abundant in the altered granite (tourmaline spheroids). The fluids in tourmaline crystals contain abundant CO_2 , and the fluids associated with the late stage quartz-hematite veins contain significant amounts of CO_2 , N₂ and CH₄.



Figure 6.33 Bar charts showing the H_2S , SO_2 (A), CO_2 , CH_4 and N_2 (B and C) concentrations (mole %) of fluids in samples of vein quartz from Grass Valley, Spoedwel, and Albert.

The vein quartz samples from each of the deposits have been selected and are compared in Figure 6.33 A-C. The H₂S content of vein material does not vary considerably. The fluids associated with the first vein quartz generation (GV07A8) contain the highest H₂S concentration, and the fluids in subsequent quartz generations contain slightly less H₂S. The SO₂ content of these fluids increases with time at each deposit. The fluids in the earliest quartz vein material have the lowest SO₂ values, and the highest values were recorded in the voungest quartz vein material.

The concentration of CO_2 in the veinhosted fluid inclusions overshadows that of CH_4 and N_2 , and for this reason a separate plot of just CH_4 and N_2 is shown. The fluids containing abundant CO_2 at Grass Valley also contain significant amounts of N_2 . The N_2 content of the fluids preceding the late stage CO_2 - N_2 -rich fluids at Grass Valley, increases from Speedwel (L1) to Albert (RP2 27).



Figure 6.34 Bar charts showing the Ar concentration (mole %) in samples of (A) vein quartz from Grass Valley, Spoedwel and Albert and (B) hypersolvus and subsolvus granites.



Figure 6.35 Bar chart showing the difference in concentrations of the major volatiles in hypersolvus and subsolvus granites The Ar content of the fluids in vein quartz follows a similar pattern to SO₂. At each deposit, the earliest fluids have the lowest concentration of Ar. In addition, there is an overall increase in Ar in the fluids associated with quartz veins from Grass Valley, to Spoedwel and Albert.

The Ar content of the host granites varies depending on the nature of the granite. The hydrothermally altered Nebo Granite (or Coarse-grained Klipkloof Granite) contains no Ar, and the hypersolvus granite at Spoedwel contains only a small amount of Ar. The fluids associated with the subsolvus granites at Grass Valley (MF3a), Albert (RP2 29), and Leeufontein (WG03, WG35 and WG43), contain progressively greater amounts of Ar.

The hypersolvus and subsolvus granites can be differentiated in terms of their volatile content. The hypersolvus granite (Nebo) contains virtually no SO₂, while the subsolvus granites contain small amounts of SO₂ and H₂S. In addition, N₂ is not as abundant in the hypersolvus as it is in the subsolvus granites.



Figure 6.36 Bar charts showing the H_2S , SO_2 (A) CO₁, CH₄ and N₃ (B) concentrations (mole %) of fluids in samples of fluorite.



Figure 6.37 Bar charts showing the H_2S , SO_2 , (A) CO_2 , CH_4 and N_2 (B) concentrations (mole %) of fluids associated with mineralisation.

The fluorite at Grass Valley, Albert and Houtenbek contain greater amounts of H_2S than SO₂, while at Spoedwel no H_2S was detected.

The late stage fluorite at Spoedwei contains the greatest N_2 concentration of all the fluorite samples analysed. CO₂ and CH₄ at Spoedwel are minor in comparison with the concentrations measured in the fluorite sample from Grass Valley. However, it should be noted, that the fluid inclusions containing high concentrations of these components are not related to fluorite precipitation, but rather were derived from fluids associated with the younger quartz-hematite veins.

The sulphur content of fluids associated with mineralisation at Grass Valley (XGV02), Spoedwel (SP9) and Albert (RP1 11, AS25 10C) are broadly similar. Equal amounts of H₂S and SO₂ are present at Grass Valley, while H2S is more abundant in the samples containing sulphides at Spoedwel and Albert. The high SO₂ content of the duplicate analyses of AS25 10C may be due to contamination by later fluids as secondary inclusions within the sample. AS25 10C also contains large amounts of CO2. The N2, CO2 and SO₂ content of this sample compares favourably with sample XGV02.

The results of the thermal decrepitation analyses are filed in the Appendix. At Grass Valley, three distinct episodes of fluid inclusion decrepitation were recorded in samples associated with cassiterite precipitation. The lowest temperature fluids ($T_{decrepitation}$ 85 to 118°C) contain only CO₂ and N₂ molecular fragments. The first water-containing inclusions decrepitated at temperatures above 206°C, and also contained CO₂ and N₂ and H₂S/SO₂ fragments. The highest temperatures for decrepitation were at 363°C and consisted of CH₄, CO₂ and N₂ fragments.

At Spoedwel a sample of vein quartz associated with sulphide precipitation contained three main episodes of decrepitation. The first is in approximately the same range as the low temperatures fluids in the Grass valley sample associated with cassiterite (i.e. 83 °C to 100°C). These fluids contain Ar, H₂O, CO₂ and N₂ fragments. Between 138 °C and 150°C, the peaks for Ar, H₂O, and N₂ fragments return to background levels and large CO₂ peaks dominate. Another population of fluid inclusions containing Ar, H₂O, CO₂ and N₂ fragments, began to decrepitate at 245°C and continued until 300°C.

In quartz veins containing sulphides at Albert, in addition to the fluids which decrepitated between 85 °C and 110 °C (CO₂ and N₂ fragments), a broad water plateau was observed between 256 °C and 314°C. At 350°C H₂S and HCl became evident. A second generation of CO₂-bearing fluid inclusions decrepitated at 381 °C, and a third generation decrepitated at 450°C. Thus, three distinct fluids containing CO₂ are present at Albert.

Decrepitation temperatures of fluids in multiple generations of vein quartz at Grass Valley indicate that the lowest temperature fluids (85° C) are not preserved in the early quartz generations and that the maximum decrepitation temperature is 473°C. These are carbonic fluids, and no water peaks were detected. The first water peaks are preserved in the seccond quartz generation, in an assemblage that decrepitated at temperatures below 400°C, and contain Ar, CO₂ and N₂. The low temperature (80° C) fluids were detected in quartz generation 3, and contain CH₄, CO₂ and N₂. An assemblage of CO₂-rich inclusions

began to decrepitate at 194°C, and the first water and Ar peaks were observed at 250°C. A second assemblage began to decrepitate at 285°C and continued until 500°C. In the fourth quartz generation the lowest temperature aqueous inclusions were encountered (100°C). N_2 and CO_2 were liberated from an assemblage which decrepitated between 200 °C and 220°C, and a second batch of water peaks appeared 293 °C and 322°C. The last quartz generations associated with hematite precipitation contain N_2 , Ar, CO₂ and minor amounts of water. These inclusions decrepitated over a broad temperature range, beginning at 97°C and continuing until 500°C. Thus, three CO_2 generations are also preserved at Grass Valley.

DISCUSSION

The results of the quadrupole mass spectrometry show that complex gas mixtures are present in the fluids from all the study areas and that these fluids are somewhat similar at each deposit.

In terms of the subplur content, the fluids associated with mineralisation are distinguished from the subsolvus granites at the ore deposits, in that they contain greater amounts of SO₂ and H₂S than the orebodies themselves (Figure 6. 38). A possible explanation for this is that as the residual melt approached water saturation, the sulphur content was also increased by being partitioned into the residual melt. Thus, as crystallisatior of the subsolvus granites proceeds, the sulphur is incorporated into the feldspars. In addition, the high concentration of SO₂ in the fluids in these subsolvus granites compared with the low SO₂ concentrations in the barren Nebo Granite and coarse-grained Klipkloof Granite, suggests that the oxidation potential of the fluids had been increased by the time crystallisation of subsolvus granite took place. The oxidation potential of the fluids may have been increased by the introduction of an external, oxidised fluid. In the model proposed for the occurrence hypersolvus and subsolvus granites, Martin and Bonin (1976) attributed the change in textures to the incursion of meteoric water. Considering the high SO₂ concentrations in the subsolvus granite, this hypothesis does indeed seem feasible.



Figure 6. 38 SO₂ (mole %) versus H_2S (mole %) of fluids associated with the subsolvus granites, and with principalisation from Grass Valley, Houtenbek, Spoedwel and Albert.

In addition to the high SO_2 concentrations in the fluids associated with the subsolvus granites at the ore deposits, these fluids contain greater concentrations of N₂, CH₄ and CO₂ than the hypersolvus granites (see Fig 6.35). Although N₂ and CO₂ may be derived from a magmatic source, the presence of hydrocarbons in the fluid usually implies that an external (connate) fluid was introduced at some stage.

In order to determine at which stage in the paragenetic sequence the external fluid was introduced, the Ar content of the fluids was examined. Norman and Musgrave (1992) have shown that the Ar content of magmatic fluids is low compared with the Ar contents of deep (and shallow) circulating meteoric waters. In Figure 6.34, samples of hypersolvus and subsolvus granite are arranged from the first formed to the last formed. A gradual increase is observed in the Ar content from the hypersolvus granites, through to the late stage Klipkloof Granite dyke material. The subsolvus granites associated with mineralisation have intermediate concentrations of Ar, which according to Norman and Musgrave (1992) indicates mixing between magmatic and deep circulating meteoric fluids. The higher Ar content in the fluids in the fine-grained Klipkloof Granite dykes implies that the magmatic fluids were diluted by the increasing meteoric component.

The origin of the fluids can be predicted using N₂/Ar ratios (Giggenba.h, 1986). The N_2/Ar ratio in air saturated water is approximately 36, but may be as high as 50 as a result of entrained air. Crustal rocks contain low but significant concentrations of N2 that average 30ppm in basalts, 21ppm in granites, 73ppm in carbonates, 120ppm in sandstone and 602ppm in shales. In comparison, geothermal fluids associated with recent magmatic activity have $N_2/Ar > 100$ (Norman and Musgrave, 1992). N_2/Ar ratios were determined for the samples of hypersolvus and subsolvus granites, as well as for the fluids associated with mineralisation. These ratios are shown in the bar charts in Figure 6.39. No ratio could be calculated for the Nebo Granite since no Ar was detected. The ratios for vein quartz associated with mineralisation at Spoedwel and Albert fall in the range for air saturated water. The fine-grained Klipkloof Granite at Leeufontein and the subsolvus granite at Albert also fall in this range. The ratios for the late stage fluids associated with quartz-her 'e veius contain high N_2/Ar ratios. The samples associated with sulphide precipitatio... also contain higher N2/Ar ratios than that for air saturated water, possibly suggesting their magmatic gases were involved. Comparing the histograms in Figure 6.39, is appears that the quartz veins have higher N_2/Ar ratios than the granites. However, when taking into account the position of each sample within the crystallisation history of the pluton, it is evident that the early quartz vein generations associated with cassiterite precipitation contain fluids with more of a magmatic ratio than samples associated with later stage sulphide mineralisation. The granite samples for which ratios could be calculated were samples of subsolvus and transsolvus granite, where the introduction of meteoric/connate water has been shown in Chapter 4, and therefore, show lower N²/Ar ratios than quartz veins formed early in the paragenetic sequence, before the incursion of an external fluid component became significant.



Figure 6.39 Bar charts of N₂/Ar in host granites and in vein quartz associated with mineralisation.

The sulphur content of the late stage Klipkloof Granite is similar to that in the fluids associated with mineralisation and quartz veins. Binary plots of SO₂ versus H₂S are shown in Figures 6.40 to 6.43. The data points have been labelled for easy reference, and boxes drawn around samples associated with mineralisation. At Grass Valley, Spoedwel and Albert, the fluids associated with sulphide mineralisation plot in similar ranges. These fluids contain less SO₂ than the subsolvus granites that they are associated with, since the sulphur was extracted from the melt and incorporated into the sulphide minerals. The fluids post-dating sulphide precipitation are thus depleted in sulphur relative to the host subsolvus granite.

The fluids associated with late-stage fluorite precipitation at each of the deposits contain greater amount of SO_2 than the fluids associated with the sulphide assemblage. At Spoedwel and Houtenbek in particular, the late stage fluorite contains significantly more SO_2 . This enrichment in SO_2 is also observed in the late stage quartz-hematite veins at Grass Valley, Spoedwel and Albert. The source of the additional sulphur is uncertain, but it seems likely that it was transported into the system, by the same fluid associated with the elevated CO_2 , CH_4 and Ar concentrations.





SO₂ (mole %) versus H₂S (mole %) in fluids at Grass Valley.





5.41 SO2 (mole %) versus H2S (mole %) in fluids at Houtenbek and Spoedwel.









CHAPTER 7

STABLE ISOTOPES

In previous chapters, numerous lines of evidence pointing toward the involvement of an external fluid in the mineralising system have emerged. For example, during microthermometry, two distinct end member fluid types were recognised in terms of their compositions and homogenisation temperatures. PIXE analysis revealed that lower temperature fluid contain significant amounts of a variety of metals, in contrast with the relatively barren, higher temperature fluid. The volatile composition of the metal charged fluids (determined by quadrupole mass spectrometry and Raman spectroscopy), indicated the presence of N_2 , CH₄ and CO₂, the concentrations of which increase with time, being more abundant in the late stage veins and aplite dykes. In addition, a steady increase in Ar contents in the fluids was observed, along with N_2/Ar ratios which indicate the presence of N_2 derived from both magmatic and meteoric origins. Thus, a study of stable isotopic signatures of the fluids associated with mineralisation in the Bushveld granite was undertaken, in order to provide unambiguous evidence regarding the origins of fluids and the validity of fluid mixing.

OVERVIEW

The application of stable isotope geochemistry to ore deposit research has been based on an understanding of mechanisms, and magnitudes of isotopic fractionation that accompany various geological processes; such as knowledge of equilibrium isotopic fractionation factors between compounds as a function of temperature and other geochemical parameters and the kinetic effects accompanying a conversion of one substance to another under a variety of conditions (Ohmoto, 1986).

H, O, C and S isotepet, provide useful information on aspects of ore forming processes which include: the situal conditions of ore formation; the origin and mass of ore forming fluids, geometry of plumbing systems, duration of hydrothermal activity; sources of ore constituents (especially sulphur, carbon and metals); redox state, metals/sulphide ratios, pH, and CO₂/CH₄ ratios; mechanisms of metal and sulphur transport and ore deposition; and the origin and evolutional processes of ore-forming magmas. However some isotopic systems are more useful than others in particular circumstances. Sulphur isotopes are generally more useful in constraining formational temperatures of sulphide ore deposits, while analysis of hydrological aspects of ore formation rely more heavily on H and O isotopic data. Sulphur and C isotopes assist in understanding chemical aspects of ore formation (Ohmoto, 1986).

Hydrogen and Oxygen Isotopes

The origin of ore-forming fluids and the hydrologic nature of plumbing systems has been estimated by comparing the H and O isotopic compositions of ore forming fluids with those of natural waters such as sea water, meteoric water, magmatic water, connate water and metamorphic water, and by comparing the H and O isotopic compositions of minerals and rocks surrounding ore deposits with those of "normal" rocks (Ohmoto, 1986).

 δD and $\delta^{18}O$ of fluids may be determined by extracting fluids from inclusions in minerals (Rye and O'Neil, 1968), or by determining δD and/or $\delta^{18}O$ of a mineral and then calculating the δ value of the fluid, using an estimated temperature of mineralisation and an equation for the isotopic fractionation factor between the mineral and H₂O.

According to Clayton *et al.*, (1989), uncertainties in mineral-water fractionation factors make it difficult to estimate the oxygen isotopic compositions of hydrothermal fluids in ore deposits. Differences of 1 to 2‰ between experimental and theoretically calculated estimates of fractionation factors imply that an uncertainty of that magnitude is introduced in the estimate of the isotopic compositions of hydrothermal fluids.

Experimental determinations of equilibrium oxygen isotopic fractionation has been carried out for quartz-water (O'Neil and Clayton, 1964; Clayton *et al.*, 1972, Matsuhisa *et al.*, 1979; Matthews and Beckinsale, 1979; and Clayton *et al.*, 1989). Linear equations defined by least-squares regressions have been published by Clayton *et al.* (1972) (Equation 1), Matsuhisa *et al.* (1976, 1978)(Equation 2) and Matthews

and Beckinsale (1979) (Equation 3) for the temperature range 200 °C to 500°C. By substituting an appropriate temperature T in the equation, solving for α , and then substituting the value for α in Equation 4, the δ value of the water may be determin x.

Clayton et al. (1972): $10^{3} \ln \alpha = 3.38 \times 10^{6} T^{-2} - 2.90$ (1) Matsuhisa et al. (1976, 1978): $10^{3} \ln \alpha = 3.31 \times 10^{6} T^{-2} - 3.26$ (2) Matthews et al. (1979): $10^{3} \ln \alpha = 3.05 \times 10^{6} T^{-2} - 2.09$ (3)

$$\alpha_{\text{quartzwater}} = \frac{1000 + \delta_{\text{quartz}}}{1000 + \delta_{\text{water}}}$$
(4)

In addition, the effect of fluid chemistry on mineral-water fractionation factors introduces another degree of uncertainty. Truesdell (1974) and Ohmoto and Oskvareck (1985) suggest that salinity has a significant effect on O isotopic fractionation factors. Oxygen isotope fractionation factors between minerals and aqueous solutions may vary by as much as $3\%_0$ at temperatures as high as 600° C, depending on solute chemistry. A similar salinity-dependent effect was suggested for H isotopic fractionation factors with errors as large as $10\%_0$ in the temperature range 150 to 300° C (Kazahaya and Matsuo, 1986).

The isotopic signatures of fluid inclusions are less problematic, provided that the minerals hosting the inclusions are non-oxygen bearing minerals. If the host mineral contains oxygen, isotopic exchange occurs between the host crystal and the fluids, thus producing incorrect values of δ^{18} O for the original fluid. Therefore, quartz is an unsuitable mineral on which to analyse fluid inclusion stable isotopic signatures. Interpretation of data involves simple comparison with experimentally determined ranges of values for fluids derived from particular sources. Figure 7.1 shows the approximate δ^{18} O/ δ D ranges for magmatic water, meteoric water, organic water, unetamorphic water and sea water, as well as the mixing trends between magmatic and meteoric waters.



Figure 7.1 Isotopic compositions and fields for sea water recoric water, primary magmatic water, metamorphic water and organic water. The kaolinite weathering line is given for reference. The ¹⁸O-shift trends due to water rock interaction and exchange in hydrothermal systems are shown for sea water and meteoric waters of compositions A and B (After Sheppard, 1986).

Seawater, meteoric water and juvenile water (water derived from the mar de that has never existed as surface water) have been termed reference waters because they have uniquely defined isotopic composition at their source. All other types of subsurface waters (i.e. connate, geothermal, metamorphic, magmatic, organic and ore-forming waters) are considered to be derived from one or more reference waters. The H and O isotopic composition of present-day seawater is relatively constant ($\delta D = 0 \pm 10\%$

and $\delta^{18}O = 0 \pm 1\%_0$). The δD and $\delta^{18}O$ values for meteoric water are linearly related, and are approximately -70‰ for δD and -10‰ for $\delta^{18}O$ in most places. The δ values become more negative with increasing distance from the sources of water vapour in the atmosphere. The estimated values for juvenile waters are $\delta D = -65\pm20\%_0$ and $\delta^{18}O$ = $6\pm1\%_0$. Juvenile water is distinguished from magmatic water (water that has coexisted with magma at some stage) in that it was derived from the mantle and has never existed as surface water.

The δD and $\delta^{18}O$ of hydrothermal fluids, pore fluids and connate waters, sedimentary basin brines, metamorphic fluids and magmatic waters deviate significantly from those of the reference waters. These deviations may results from the formation of hydrous minerals, shale membrane filtration, fluid mixing and unmixing, and isotopic exchange with rocks (Ohmoto, 1986). Most geothermal fluids have δD values identical to the local meteoric water but are enriched in $\delta^{18}O$. The magnitude increases with temperature and salinity of the fluid, and is interpreted by Craig (1963) to mean that the fluids were merely recycled meteoric waters, which had acquired heat and salts, and exchanged O isotopes with deeply buried rocks.

In sedimentary brines, the δD and $\delta^{18}O$ values increase with increasing temperature and salinity. A wide range of values have been recorded for brines in different sedimentary basins ($\delta D = -150$ to 20\% and $\delta^{18}O = -20$ to 10\%), but in any one basin the values are relatively uniform. The isotopic composition of metamorphic fluids (fluids formed by dehydration of minerals during regional metamorphism) vary from one area to another depending on the initial rock type and the history of water-rock interaction. The range for metamorphic waters is approximately $\delta D = 0$ to -70% and $\delta^{18}O = 3$ to 20\%. The typical range for magmatic fluids is $\delta D = -75$ to -30% and $\delta^{18}O = 7$ to 13\%, and is strongly induced by the type of rock that is partially melted.

In Figure 7.1, the term "organic waters" refers to the waters whose D/H ratio is derived from the direct or indirect transformation of organic matter, bitumen, coal, kerogen, petroleum, organic gases, etc. by processes such as dehydration, dehydrogenation oxidation and/or exchange (Sheppard and Charef, 1986). The range for H in these waters is $\delta D = -90$ to -250%, while the $\delta^{18}O$ values are determined by the reservoir rocks and the temperature of exchange, and are similar to metamorphic water values (Sheppard, 1986).

Carbon isotopes

Carbon isotopes have not been used as extensively as hydrogen, oxygen and sulphur isotopes in the study of ore deposits because carbon-bearing minerals usually post-date the main stages of mineralisation (Ohmoto, 1986). Apart from being components of the atmosphere and oceans, fixation of carbon species as limestone, and organic matter is common. δ^{13} C values of modern marine limestone fall in the range -1 to 2% (average 1%) and for marine organic carbon in the range -30 to -10%. Methane produced by biogenic reduction of HCO₃⁻ near the sediment water interface has values between -110 and -55%. Thermal decomposition is the primary source of natural gas at temperatures greater than 50°C. Σ^{12} C values of CA₄ formed by thermal cracking are between -55 and -35%. CO₂ generated by thermal decomposition of organic matter may have been an important source of carbonate in some sediment-hosted sulphide deposits. The δ^{13} C values of aqueous carbonate produced by dissolution or thermal decarbonatisation fall in the range -8 to 4%. The isotopic signatures of carbon which has been derived from the above mentioned sources are shown in Figure 7.2.



Increasing Temperature

Schematic diagram showing δ^{13} C values of carbon-bearing compounds Figure 7.2 in near surface environments (after Ohmoto, 1986),

As with δD and $\delta^{18}O$, the $\delta^{13}C$ value is diagnostic of its source. The $\delta^{13}C$ values of ΣCO_2 can be calculated from the $\delta^{13}C$ of the carbonate mineral using 1) fractionation factors between the mineral and H₂CO₃ (CO₂ + H₂CO₃) or HCO₃⁻ and between aqueous carbonate species, and 2) the relative abundance of H_2CO_3 and HCO_3^- in the fluid. Fractionation factors are a function of temperature only because the assumption of isotopic equilibria in carbonate species is usually valid (Ohmoto, 1986).

Stable isotopes in meteoric-hydrothermal systems

In modern meteoric-hydrothermal systems on continents and islands, virtually all the water is of meteoric origin (Craig et al., 1956). Although the δ^{18} O and δD values of meteoric water are linearly related, the δ^{18} O values of the geothermal waters are higher than the local meteoric waters. This ¹⁸O-shift reflects isotopic exchange between heated meteoric waters and ¹⁸O-rich rocks, which, after interaction, become depleted with respect to ¹⁸O. As a result of the very large mineral-water fractionation factors,

the 18 O/ 16 O ratios of the rocks can be increased by low temperature interactions with meteoric waters, as observed during weathering and in the low temperature parts of some meteoric-hydrothermal systems (Criss *et al.*, 1984). The actual response of isotopic systems to fluid rock exchange depends on the initial isotopic composition of the fluid and rock, on the temperature as reflected by the water-rock fractionation factor, on the relative proportions of fluid and rock involved in the exchange, on the degree of approach to isotopic equilibrium, and on the boundary conditions (Criss and Taylor, 1986).

Oxygen isotopic studies have identified a number of areas where ancient meteorichydrothermal system have caused pervasive and widespread alteration, isotopic exchange and often economically significant mineralisation. The most important epithermal deposits are simple fissure veins of quartz or chalcedony containing precious metals (Au/Ag) that may be free or associated with sulphide minerals. Other epithermal deposits are valued for base metals, mercury, antimony, and alunite. They may occur as stockworks and pipes, below impervious zones and in subhorizontal stratigraphic beds (Criss and Taylor, 1986). The δD and $\delta^{18}O$ values for fluids associated with these epithermal deposits usually plot very close to the meteoric water line, or to the right, reflecting the ¹⁸O-shift observed in modern geothermal waters. Other examples of one deposits formed by the meteoric hydrothermal fluids include the Pb-Zn replacement hodies at Bluebell, British Columbia (Ohmoto and Rye, 1970), and the rich Main Stage veins at Butte (Sheppard and Taylor, 1974), where relatively high salinities and temperatures were recorded. At Climax, Colorado, meteoric waters were involved in the formation of the Mo porphyry (Hall *et al.*, 1974)

Studies of the light stable isotopes associated with mineralisation in the Bushveld gravites has received very little attention to date. The only reference literature available is an oxygen isotope study by Pollard *et al.* (1991) at the Zaaiplaats Tin Mine. Pollard *et al.* (1991) found that whole rock samples from the Zaaiplaats Tin Mine had oxygen isotopic compositions between 9.2 and 9.9 per mil. The δ^{18} O values of quartz from granites and the marginal pegmatite range from 7.3 to 9.4 per mil, whereas those of quartz from cavities, low-grade ore bodies, pipes and veins range from 7.8 to 13.5 per

mil (Pollard *et al.* 1991). Pollard *et al.* (1991) modelled the isotopic exchange between granites and magmatic fluid phase in isotopic equilibrium with average Bobbejaankop Granite quartz at 600°C and found that whole rock compositions result from final exchange at temperatures less than 400°C, with fluid compositions in the range 4.2 to 5.2 per mil at 300°C and 0.8 to 1.8 per mil at 200°C. Pollard *et al.* (1991) maintain that these results are consistent with fluid compositions calculated from δ^{18} O and pressurecorrected fluid inclusion homogenisation temperatures, and indicate that oxygen isotope variation at Zaaiplaats reflects exchange between the granite and the magmatic fluid phase at temperatures down to 200°C.

EQUIPMENT AND METHODS

The oxygen isotopes of quartz, as well as carbon, oxygen and hydrogen isotopes, of fluid liberated from fluid inclusions from the Grass Valley, Spoedwel, Houtenbek and Albert deposits were analysed at the Department of Geological Sciences, University of Michigan. The procedure is described by Vennemann and O'Neil (1993). A schematic diagram of the experimental set-up of the fluid inclusion line is shown in Figure 7.3.



Figure 7.3 Schematic representation of the experimental set-up for separating CO₂, CH₄, H₂O liberated from fluid inclusions.

The fluid inclusion contents were released from the sample by gradual heating within a furnace. The fluid inclusion line at the Deptartment of Geological Sciences, University of Michigan, is designed in such a way that all CO_2 , CH_4 and H_2O liberated from each sample can be trapped and the C, O and H isotopic signatures determined. Initially, the H_2O and CO_2 released is frozen into a U-tube cold trap, and the other gases, chiefly CH_4 are allowed to pass through the CuO_2 chamber. The CH_4 is converted to H_2O and CO_2 , which is subsequently frozen into the U-tubes behind the CuO_2 chamber. The CO_2 is separated out first and collected in a 6mm Pyrex safety tube, which is then removed from the line for analysis. The water is released next and is trapped in a quartz tube containing Zn. Zinc is used to react with the water on heating, producing ZnO and H_2 . The tubes are then cracked under vacuum on the mass spectrometer and the hydrogen isotope composition analysed.

 CO_2 is liberated from the U-tube containing H₂O and CO₂, frozen into a Pyrex tube and removed from the line. The water is then trapped in a detachable cold finger and stored in a water bath for two days, to allow for equilibration of ¹⁸O and ¹⁶O.

SAMPLE MATERIAL

Samples of non-oxygen-bearing minerals (i.e. fluorite and sphalerite) were selected for analysis of the isotopic signatures of fluid inclusions. One quartz sample was included for comparison. The samples are tabulated in Table 7.1. With the exception of SP2, the samples were prepared by separating the fluid inclusion-bearing host minerals from the feldspar and other rock forming minerals by means of magnetic separation and hand picking. Insufficient sample material of fluorite from Albert Silver Mine could be gathered, and, therefore, no analyses could be made.

DEPOSIT	SAMPLE	SIZE (g)	CHARACTERSITICS		
Spoedwel	SP2	17.99	Interstitial fluorite and quartz (whole much).		
	SP13	3.75	Massive fluorite post-dating sulphide mineralisation		
Grass Valley	GV02	3.82	Quartz		
	GV08	5.91	Finorite filling a vug in granite		
Houtenbek	HBF	9.6	Purple fluorite		
· · · · · · · · · · · · · · · · · · ·	ZNS	9.65	Sphalerite		

 Table 7.1
 List of samples chosen for isotopic analysis of fluid inclusion decrepitates.

The quartz samples analysed for δ^{18} O are listed in Table 7.2. The samples were chosen specifically to represent fluids associated with barren hypersolvus (samples NEBO and BBK1) and subsolvus granites at Albert (RP2 29) and Grass Valley (MF3a), as well as the fluids associated with cassiterite mineralisation (GV02), and late stage quartz-hematite veins (GV01a and b) at Grass Valley. Admittedly, one sample of mineralisation is not representative, but problems encountered with H₂S liberated from mineralised samples inhibited extensive analysis of such sample material.

Table 1.5 Dist of Sumples subset for white parches and the	Table 7.2	List of samples chosen	for oxygen isotor	e analysis of quar	tz.
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SAMPLE	CHARACTERISTICS
GV01a	Second generation of quartz filling fracture at Grass Valley.
GV0Ib	First generation of quartz filling fracture at Grass valley.
GV02	Quartz associated with hydrothermal cassiterite at Grass Valley.
BBKI	Hydrothermally altered Nebo Granite (Bobbejaankop granite equivalent).
RP2 29	Coarse-grained subsolvus granite from Albert Silver Mine.
NEBO	Unaltered Nebo Granite.
MF3a	Medium-grained subsolvus granite from Grass Valley.

RESULTS

Table 7.3

SP13

72.1

The δ^{18} O and δ D values from fluid inclusions are shown in Table 7.3. The δ values from the fluid inclusion H₂O are shown in the first two data columns, and the δ values from the water converted from CH₄ are shown in the second two data columns. The δ^{18} O of samples GV02 and SP2 should be treated with caution, since they were derived from quartz-hosted fluid inclusions. However, the δ D values of these samples are reliable. Unfortunately, in some of the samples where CO₂-rich fluid inclusions are abundant, both δ^{18} O and δ D values were not obtained because one or other of the isotopes was not detected. The samples where both values were obtained are plotted in Figure 7.4. The δ values associated with mineralisation and fluorite at Houtenbek and Grass Valley have similar δ^{18} O signatures, but the δ D values vary between -52 and -96 ‰. The values obtained from water converted from methane for the fluorite at Grass Valley plot separately.

methane.					
SAMPLE	δ ¹⁸ O _{water} (%0)	δD water (%0)	δ ¹⁸ O methanet (%)	$\delta D_{methane}(\%)$	
HBF	1.2	-52.7	21.4	not detected	
ZNS	1.6	-93.0	55.6	not detected	
GV02	1.0	-96.2	15.5	not detected	
GV08	17.5	not detected	19.1	-150.6	
507	not detected	-60.8	not detected	-167.3	

Stable isotopic data for δ^{13} O and δ D from fluid inclusion water and

not detected

not detected

302

not detected



Figure 7.4 δ^{18} O and δ D values from fluid inclusion water (=) and water converted from methane (X) for samples from Houtenbek, and Grass Valley.

The results of the δ^{18} O determinations of quartz from host granites, and quartz associated with veins and mineralisation are shown in Table 7.4. Calculations of the δ^{18} O fluid using the equations of Clayton *et al.* (1972) and Matsuhisa *et al.* (1979) for T= 300°C are also tabulated. Figure 7.5 plots the measured δ^{18} O_(quartz) values and the calculated δ^{18} O fluid (Matsuhisa *et al.*, 1979). The host minerals cluster together at lower values of δ than the fluids associated with mineralisation and late stage quartz veins.

Table 7.4 $\delta^{18}O_{(quarte)}$ and $\delta^{18}O_{(finid)}$ values for quartz . $\delta^{18}O_{(finid)}$ % values were calculated using the equations of Clayton *et al.* (1972) and Matsuhisa *et al.* (1979) for T= 300°C.

SAMPLE	δ ¹⁸ Oquariz %00	δ ¹⁸ Ο finid %oo	δ ¹⁸ O fisid %
· .		Clayton et al. (1972)	Matsuhisa e al. (1979)
GV01a	10.28	3.34	3,38
GV01b	10.34	3.40	3.44
GV02	10.14	3.20	3.24
RP2 29	7.31	1.12	1.15
MF3a	8.51	0.39	0.43
BBK1	8,04	1.22	1.25
NEBO	8.14	1.59	1.62



Figure 7.5 Graph of $\delta^{18}O_{\text{quartz}}$ versus $\delta^{18}O_{\text{water}}$ of unmineralised host granites and quartz associated with veins and mineralisation at Grass Valley.

The δ^{13} C values obtained from fluid inclusion CO₂ are shown in Table 7.5 DI-CO₂ values represent the CO₂ used for determining the fractionation factor between fluid inclusion CO₂, and CO₂ standard. The δ^{18} O values of the CO₂ are also shown in Table 7.5. The data are plotted in Figure 7.6. The δ^{13} C values fall in the range of approximately -8 to 3.5%. The samples of late stage fluorite from Spoedwel an⁴. The late is enriched in δ^{18} O relative to the fluorite samples is m⁴. The bek and Grass Valley.

Table 7.5 δ^{13} C and δ^{18} O from CO₂ in fluid inclusions from Houtenbek, Grass Valley and Spoedwel.

HBR CC DI ZNS CC), -CO ₂),	-7.5 -3.9	21.4 38,1	
DI ZNS CC	-CO <u>3</u> Di	-3.9	38.1	
ZNS CC),			
	- 2	1.4	55.6	
124	-CO.	-3.4	40.1	
SP13 CC	D ₂	2.4	72.1	
DI	-CO ₂	?	?	
GV02 CC	01	-2.5	15.6	
DI	-CO ₂	-3.8	39.1	
GV08 CC	02	3.5	17.8	
DI	-CO2	-30.8	19.1	


Figure 7.6 Plot of δ^{13} C and δ^{18} O from CO₂ in fluid inclusions from Houtenbek, Grass Valley and Spoedwel.

DISCUSSION

Oxygen and Hydrogen Isotopes

The results of this study are consistent with those of Pollard *et al.* (1991) which are summarised in Figure 7.7. Calculations of δ^{18} O flatd at 300 °C (at lower temperatures, errors in fractionation factors are unacceptable) using the equations of Clayton *et al.* (1972) an Matsuhisa *et al.* (1979) yielded values in the same ranges as found by Pollard *et al.* (1991) for the low temperature hydrothermal quartz. Furthermore, the oxygen isotopes indicate that the fluids associated with crystallisation of the Nebo Granite and the hydrothermally altered Nebo Granite (Bobbejaankop Granite equivalent) can be distinguished from the subsolvus granites and from late- stage quartz veins associated with mineralisation (Figure 7.5). The subsolvus Verena Granites hosting the Albert Silver deposit have the lowest δ^{18} O quartz value (7.31per mil), followed by the Bobbejaankop Granite (8.04 per mil), Nebo Granite (8.14 per mil) and subsolvus granite from Grass Valley (8.51 per mil). The hydrothermal quartz associated with hydrothermal cassiterite at Grass Valley and late-stage quartz veins associated with hematite precipitation have values which are considerably higher (10.14, and 10.28 to 10.34 per mil, respectively). The ranges of δ^{18} O values obtained from quartz, as well as the calculated values of $\delta^{18}O_{\text{fluid}}$ (at 300°C) are compared with the data of Pollard *et al.* (1991) in Figure 7.7. The data from Zaaiplaats are indicated by the narrow lines, while the data obtained in this study are indicated by heavy lines. The boxed captions indicate $\delta^{18}O$ values from quartz and the others indicate ranges for fluids.



Figure 7.7 Comparison of δ^{18} O fluid and δ^{18} O quartz (narrow lines) from Zaaiplaats (Pollard *et al.*, 1991) and the Grass Valley, Albert, Houtenbek and Spoedwel deposits (this study) (heavy lines).

It appears that the fluids have become enriched in ¹⁸O with time. However, the depletion of ¹⁸O in the host granites compared with the enrichment of ¹⁸O in the fluids associated with mineralisation and late stage quartz veins, is reminiscent of the ¹⁸O-shift described in meteoric-hydrothermal systems. Furthermore, the gradual enrichment of ¹⁸O in fluids of hydrothermal systems was interpreted by Mullis *et al.* (1994) as

indicating retrograde fluid evolution, which is controlled by uplift and cooling, and the involvement of meteoric water.

Evidence for the involvement of meteoric water is provided by comparing the data points with established δ ranges for fluids derived from different sources (Figure 7.8). The fluids associated with sulphide mineralisation, such as those trapped within sphalerite at Houtenbek, plot in between the meteoric water line and the field for primary magmatic water. Fluids that plot in this area of the graph are derived from mixing of meteoric and magmatic fluids. The $\delta D/\delta^{18}O$ plot of fluids associated with mineralisation (Figure 7.8) shows a large range of δD values, but $\delta^{18}O$ remains relatively constant. According to Taylor and O'Neil (1977) this trend reflects an increasing component of meteoric water. High δD values imply the involvement of connate water. The late-stage purple fluorite from Houtenbek shows the highest δD values and fluids associated with sulphide mineralisation have lower δD values. Thus, the δD values became progressively more positive with time, as the external fluid component became more dominant.





Carbon Isotopes

The carbon isotopic signatures prove irrefutably that an external fluid component was introduced into the system. The majority of values indicate that the carbon was derived from a carbonate source (Figure 7.9). The fluorite at Grass Valley and Spoedwel, as well as the sphalerite at Houtenbek, contains C which was derived from a carbonate source. The fluorite from Houtenbek falls in the overlap between mantle derived fluids and carbonate derived fluids. Since no evidence for C derived from an external organic carbon reservoir was found, and considering that the geological setting of the Houtenbek deposit suggests that it represents a hydrothermal vent, the C in sample HBF is interpreted as being mantle derived.



δ¹³C

Figure 7.9 δ^{13} C data points indicated relative to ranges of values given by Ohmoto (1986) for C derived from an external reservoir, mantle or carbonate source.

CHAPTER 8

SYNTHESIS AND MODEL

The results of this study on the nature of hydrothermal fluids associated with granitehosted mineralisation in the eastern lobe of the Bushveld granites has revealed that fluid mixing was a major factor governing the deposition of metals in favourable structural traps within the granites and surrounding country rock.

In the previous chapters, various analytical techniques have shown that the associated hydrothermal fluids are complex mixtures of various metals and volatiles, which were derived from at least two different sources, one being magmatic and the other an external meteoric/connate source.

Evidence pointing towards a fluid component of a magmatic origin includes the following:

- N₂/Ar ratios in the range stipulated by Norman and Musgrave (1992) for fluids of magmatic origin.
- A gradual increase was observed in the Ar content in fluids from the hypersolvus granites, through to the late stage Klipkloof Granite dyke material. The higher Ar content in the fluids in the fine-grained Klipkloof Granite dykes implies that magmatic fluids were progressively diluted by an increasing meteoric component (Norman and Musgrave, 1992).
- Two of the major factors governing the formation of fluorite deposits are the dilution of mineralising fluids by ground water and the change in temperature gradient on contact with excess groundwater (Deer *et al.*, 1962). However, Plumlee *et al.* (1995) have shown that the interaction of magmatic fluids/gases with Ca, Mg and SO₄-rich brines results in the formation of acidified brines which precipitate fluorite on cooling from 150°C to 140°C. Progressive mixing of this brine with the original brine leads to further precipitation of significant amounts of fluorite. The model proposed by Plumlee *et al.*

(1995) involves the migration of magmatic gases upwards and along fractures in the crystalline basement, where titration of these gases into basinal brines at depth led to preferential mineralisation of these structures. Similarly, in the Bushveld granites, basinal brines, which were channelled along regional fractures, interacted with the magmatic fluids and precipitated fluorite at temperatures between 300°C to 150°C. According to Plumlee *et al.* (1995), a second episode of fluorite precipitation takes place at lower temperatures (<150°C) The presence of two generations of fluorite associated with mineralisation at Spoedwel and Albert, which were formed at similar temperature conditions as that found by Plumlee *et al.* (1995), suggests that fluid mixing was responsible for the precipitation of the fluorite, and is assumed to be an important factor in the development of sulphide and fluorite-hematite assemblages.

Copper was detected by PIXE analysis in Type 5b (CO2-rich) fluid inclusions, which is consistent with the theory that copper is transported in the vapour phase (Heinrich *et al.*, 1992). Thus, the source of copper in the fluids is most likely magmatic, and migrated with HF-rich gases emanating from the crystallising magma.

The external fluid component was derived from two sources, namely, a meteoric source and a connate source. The fluid inclusion studies clearly indicated that two distinctly different fluids coexisted at similar temperatures in quartz associated with the sulphide paragenesis. The fluid inclusion evidence for the mixing of two fluids include:

- Variable phase proportions, wide ranges of homogenisation temperatures and wide ranges of final melting temperatures within single fluid inclusion assemblages indicate that entrapment of a heterogeneous fluid took place.
- Dissolution of halite daughter crystals after homogenisation of the liquid and vapour phases indicates that the heterogeneous fluid was the result of fluid mixing rather than boiling.

- The overlap of homogenisation temperature ranges of saline and non-saline fluid inclusion assemblages in the first fluorite generation implies that both fluids were circulating at the same time and that mixing probably took place.
- The presence of two distinctly different fluid inclusion assemblages (one highly saline and the other relatively unsaline) coexisting a similar temperatures indicates the presence of two contrasting parental fluids.
- The fluids associated with the sulphide assemblage became progressively more saline, peaking with the deposition of sphalerite, and then decreasing in salinity with the precipitation of chalcopyrite. The high salivity of the external fluid suggests that the source of this fluid was not purely meteoric, but rather, that it was a basinal brine or connate fluid, derived from the Transvaal sedimentary rocks into which the granites were intruded. Thus, initially, mixing between a magnatically derived fluid and a connate fluid occurred. The magnatic fluids waned, the connate fluid became the dominated the system, but as the magnatic fluids waned, the connate fluid became the dominant fluid, which is reflected by the increasing salinity of the fluids from the precipitation of arsenopyrite to sphalerite. Thereafter, the fluids became progressively less saline as dilution of the magnatic and connate fluids by meteoric fluids, which entered the system along fractures in the granite, proceeded.
- Two distinct fluid types have been detected in terms of their solute composition. These fluid types may be correlated with the two end-member fluids recognised during microthermometry. The fluids with the lowest salinity and highest temperature are those which PIXE analysis has shown to be relatively barren with respect to ore-forming components. These fluids are represented by the early fluids rt Grass Valley which precede cassiterite precipitation. In contrast, the highly saline, lower temperature fluid preserved in primary inclusions hosted by a second generation of quartz at Spoedwel contain significant amounts of all the ore-forming components. The sample material from Albert represents the intermediate category of fluids recognised by microthermometry, where the temperature and solute content is moderate, reflecting partial interaction between the two parental fluid types.

- The fluid inclusions from Grass Valley associated with the precipitation of hydrothermal cassiterite and small amounts of galena, sphalerite and chalcopyrite contained CO₂ ± N₂±CH₄. Thus, these gases were certainly present in the fluids associated with Stage 2 (i.e. the precipitation of the sulphide assemblage) in the paragenetic sequence.
- The high concentration of SO₂ in the fluids in the subsolvus granites compared with the low SO₂ concentrations in the barren Nebo Granite and coarse-grained Klipkloof Granite, suggests that the oxidation potential of the fluids had been increased by the time crystallisation of subsolvus granite took place.
- The fluids associated with subsolvus granites are less saline than the hypersolvus granite fluids, providing supporting evidence that the incursion of meteoric water triggered the change from hypersolvus to subsolvus granite textures, and that the magmatic fluids were diluted by meteoric/comate fluids.
- N₂/Ar ratios indicate that nitrogen from both magmatic and meteoric sources is present in the fluids associated with mineralisation and in late stage quartz veins. The ratios for vein quartz associated with mineralisation at Spoedwel and Albuit fall in the range for air saturated water. The fine-grained Klipkloof granite at Leeufontein and the subsolvus granite at Albert also fall in this range. The ratios for the late stage fluids associated with quartz-hematite veins contain high N₂/Ar ratios. The samples associated with sulphide precipitation also contain higher N₂/Ar ratios than that for air saturated water, possibly suggesting that magmatic gases were involved.
- Sphalerite precipitation at Grass Valley, Albert, and Spoedwel occurred over a temperature range of approximately 100°C, but the compositions of the fluids were very similar. Assuming that mineralisation was triggered by mixing of two fluids, the similar fluid compositions associated with sphalerite deposition suggests that fluid mixing occurred at different stages in the paragenetic sequences.

- Although N₂ and CO₂ may be derived from a magmatic source, the presence of hydrocarbons, such as CH₄ and C₂H₅ and C₃H₈, in the fluid usually implies that an external fluid (meteoric and /or connate) was introduced at some stage.
- At Spoedwel and Houtenbek in particular, the late stage fluorite contains significantly more SO₂ than H₂S. This enrichment in SO₂ is also observed in the late stage quartz-hematite veins at Grass Valley, Spoedwel and Albert. The source of the additional sulphur is uncertain, but it seems likely that it was transported into the system, by the same fluid associated with the elevated CO₂, CH₄ and Ar concentrations.
- High δD values and the enrichment in $\delta^{18}O$ with time indicate the involvement of meteoric/connate water.
- The fluid inclusions hosted by quartz and tourmaline in the tourmaline spheroids show that Fe, Zn and Pb (as well as trace elements- Br, Ga, Rb, Sr) are present in the late stage fluids. The presence of these elements in the fluids at such a late stage in the system suggests that, in addition to enrichment of the residual fluid in incompatible elements, some of these components may have been leached from the Transvaal Supergroup and transported into the Bushveld granites by the connate fluid.
- The majority of δ^{13} C values indicate that the carbon in the fluids was derived from a carbonate source. The Malamani dolomites of the Transvaal Supergroup, into which the Bushveld granites were intruded, are thus a possible source of some of the carbon introduced by the external fluid.

Thus, fluid inclusion studies of the fluids associated with the various stages of mineralisation in the eastern lobe of the Bushveld complex have demonstrated that magmatic, meteoric and connate fluids were involved in the mineralising process. Further evidence of the interaction between these fluids, recognised during mineral petrography, include:

Petrographic studies of the graphics hosting mineralisation in the eastern lobe of the Bushveld Complex have revealed that these granites can no longer simply be described as hypersolvus granites. In addition to hypersolvus granites, subsolvus and transsolvus granites have been also been recognised, the implications of which are significant in constructing any model for the evolution of the Bushveld granites and associated mineralisation. The hypothesis proposed by Martin and Bonin (1976) to explain the hypersolvus-subsolvus granite association incorporates the concepts of water saturation of the magma, with the ingress of meteoric water as the circulation of magmatic fluids wanes. The petrographic evidence (nuscovitisation, local fusion of perthites, albitisation of feldspar, and precipitation of late albite) suggests that water saturation occurred during the final stages of the crystallisation of the hypersolvus granite, coinciding with the onset of subsolvus granite crystallisation. This is supported by evidence from Ollila (1981), who conducted a study of the structural state and composition of the alkali feldspars in the Bushveld Granites, and found that the alkali feldspars in the Bobbejaankop Granite (coarse-grained Klipkloof Granite) exhibit the highest degree of ordering and are maximum microcline, indicating the lowest thermal state. The alkali feldspars from the Lease Granite (Fine-grained Klipkloof Granite) are intermediate microcline, indicating a higher thermal state, or less ordered state, which is due to the rapid cooling rate of this granite (Ollila, 1981). The Nebo (or "Main") Granite alkali feldspars are monoclinic, reflecting a state of greater disorder in the lattice. Ollila (1981) explained this phenomenon as the result of volatile deficiency during initial crystal growth stages, which may have prevented the later development of triclinic alkali feldspars. The variation in the structural state of the alkali feldspars is directly related to the availability of hydrothermal fluids during their cooling history (Parsons, 1978). Thus, the absence of volatiles during the crystallisation of the Nebo Granite is reflected in the monoclinicity of the K-feldspars, even though the rate of cooling was sufficiently slow for the formation of large interlocking crystals. As the degree of fractionation of the host rock increases, the water content of the residual melt increases, causing increased order in the younger K-feldspar crystals. Thus, the higher degree of order observed in the coarse-grained Klipkloof Granite reflects the increasing water content of the residual melt. This trend would have continued during the formation of the Lease Granite (Finegrained Klipkloof Granite) were it not for the rapid cooling of this material (Kleemann and Twist, 1989).

- The overall paragenetic sequence in the Bushveld granites suggests that mineralisation took place in three discrete episodes. The first episode of mineralisation resulted in the formation of cassiterite-scheelite-wolframite-molybdenite-specularite and possibly arsenopyrite. The mineralisation is disseminated and formed by processes related to fractional crystallisation of the magma. Fluctuations in the pH of the late magmatic fluids as they interacted with the wall-rocks and with the externally derived meteoric/connate fluids channelled along the fractures, resulted in the deposition of a second episode of mineralisation, which is represented by the subbide paragenesis pyrite-galena-tetrahedrite/termantite-sphalerite-chalcoryrite. The occurrence of this assemblage is fracture-related, with sizeable deposits located on the flanks of large-scale regional faults. These fracture systems acted as conduits for mineralising fluids. As the external fluid comportent became progressively more dominant, the paragenesis changed, and deposition of hematite, pitchblende and large amounts of fluorite took place. The introduction of this third assemblage along the same fracture systems which localised the sulphide assemblage, resulted in alteration of the sulphides, to secondary minerals such as bornite, chalcocite, digenite, covellite and limonite. The extended nature of this three stage paragenetic sequence is considered to reflect widespread mixing between and an early fluid derived by H₂O-saturation of the granitic magma, and an external meteoric/connate fluid.
- The volatiles associated with the final fractionated portion of the granitic melt caused deuteric changes such as the hematitisation of the feldspars, chloritisation of mafic minerals, albitisation of perthite and precipitation of secondary albite. These deuteric changes have the effect of increasing the iron content of the fluids, priming the system for the deposition of the late-stage massive hematite in the third stage of mineralisation. The deuteric alteration marks the interface between fluids with high iron sulphide activity from those with low iron sulphide activity. The iron enriched fluids caused alteration of the primary sphalerite by ion exchange of Fe and Zn, producing iron-rich opaque sphalerite as alteration rims and fracture planes within the transparent sphalerite.

The colour of the chlorite also reflects an increase in the iron content of the fluids. Chlorite associated with sulphide mineralisation is grass-green and highly pleochroic. In contrast, the chlorite associated with the orthomagmatic cassiterite mineralisation is olive-green to brown.

- Covellite overprinting occurred at some stage after consolidation of the sulphide minerals, since alteration of the copper-bearing minerals occurs along grain boundaries and micro-fractures. This phenomenon is characteristic of retrograde processes, i.e. the older minerals remain stable while the younger ones overgrow or fill fractures, within them (Heroley and Hunt, 1992). According to Hemley and Hunt (1992), when dissolution and replacement occurs, they are the result of the imposition of a contrasting chemical environment, and not simply lower temperatures. The petrographic evidence suggests that the sulphide mineralisation followed a prograde thermal path, which was then changed to a retrograde thermal path as the external meteoric/connate fluid component became more pronounced.
- Local occurrences of hydrothermal tournaline veins and spheroids, similar to those of the Sn-W-Cu deposits of Cornwall (south-east England) (London and Manning, 1995), have been recognised in the Bushveld granites. In both cases, the interaction of boronrich, magnatically derived fluids, and Fe-Mg-rich, connate fluids is thought to have resulted in localised precipitation of tournaline

The model proposed by Kleemann (1985) (see Chapter 2) for the evolution of the Bushveld granites has been modified in Figure 8.1. The first two steps of the model are essentially the same as Kleemann's (1985) model. After emplacement of the magma, the margins of the pluton cooled rapidly and crystallised a fine-grained equivalent of the Nebo Granite. The central portions of the pluton cooled more slowly, promoting the development of large perthic and quartz crystals which are typical of the Nebo Granite. Volatile enrichment of the residual melt took place and intense hydrothermal alteration of Nebo Granite resulted in the development of the coarse-grained Klipkloof Granite.

Tensional fracturing of the pluton created conduits along which external connate and meteoric fluids where channelled into the pluton. These fractures are the sites of hydrothermal alteration, such as sericitisation, albitisation and hematitisation, and in parts of the Bushveld Complex, are related to polymetallic mineralisation. Thus, the introduction of hydrothermal fluids along these fractures, served to concentrate and localise ore-forming components.

In addition to the gradual volatile enrichment of the crystallising magma, the introduction of external fluids along fractures promoted water saturation of the magma, and the consequent crystallisation of subsolvus granites. Two generations of subsolvus, fine-grained Klipkloof Granite, which were derived from the more differentiated, water saturated melt, were intruded as dykes and sills into the crystallised to partially crystallised Nebo Granite. In places where the Nebo Granite was not completely solidified, the transsolvus Porphyritic Klipkloof Granite was formed.

The mixing of the magmatic fluids and the connate fluids caused the precipitation of the sulphide assemblage. Initially, the connate fluid component was minor, but as the magmatic fluid component in the system waned, the connate component became more dominant, and the salinity of the fluids increased, coinciding with the precipitation of the sulphide assemblage. At this point, the introduction of cool, unsaline meteoric water (blue arrows on Figure 8.1) into the system took place, diluting the remaining metal-charged mixture of magmatic and connate fluid (pink arrows on Figure 8.1), and causing precipitation of the fluorite-hematite assemblage at lower temperatures.



1

Intrusion of Nebo granite magma and formation of intrusion breecia.



Disseminated Sn mineralisation forms as a result of fractional crystallisation. Late-stage volatile-rich rest liquids (yellow arrows) interact with connate fluids (red arrows) which are claunelled into pluton along fractures.



Crystallisation of fine-grained, hypersolvus Nebo granite along margins of pluton, and coarser-grained Nebo granite towards the centre of the pluton.



Subsolvus granites form in water-saturated portions of the pluton and late-stage aplite dykes (Finegrained Klipkloof granite) are intruded into the Nebo Granite. Meteoric water (blue arrows) cuters the system along fractures.



Decending meteoric water mixed with the combined magmaticconnate fluid (pink arrows), precipitating the second and third phases of mineralisation in different settings. A Zaaiplaats. B Grass Valley C Spoedwel D Albert E Stavoreb.

Figure 8.1 Proposed model for the evolution of the Bushveld granite and associated mineralisation

The hypothesis proposed for mineralisation in the granites of the eastern lobe of the Bushveld Complex is shown in Figure 8.2, with the results of this study superimposed. The high temperature fluids recognised by Ollila (1981) and Pollard *et al.* (1991) were not encountered in this study, since the disseminated tin assemblage was not well developed at any of the deposits chosen for analysis. Since the mineralisation was vein-related, the bulk of sample material post-dated that phase when high temperature fluids were circulating. Fluid inclusions from samples of the host granites immediately adjacent to the mineral deposits had been subject to stresses associated with fracturing, and this may explain why none of the high temperature fluids were preserved in these samples. The primary fluid inclusions were probably destroyed during fracturing of the crystal, and refilled by secondary fluid generations, or sealed by subsequent quartz growth.



Figure 8.2 Diagrammatic representation of the hypothesis proposed for minara'isation in the granites of the eastern lobe of the Bushveld Complex with additional information obtained during this study superimposed.

The period of time from emplacement of the magma, through the various stages of granite crystallisation, and three phases of mineralisation was determined by radiogenic isotopic studies to have spanned approximately 1000 m.y. From the time of emplacement of the Nebo Granite magma at 2054 Ma (Walraven, 1993), the radiogenic isotopic systems were exposed to disturbances caused by hydrothermal activity between 1600 Ma and 1700 Ma, as well as at 400 Ma (Robb *et al.*, 1994).

Ages for the closure of lead isotopic systems vary. At Zaaiplaats in the northern part of the complex, internal exchange of Pb ceased after 1100 Ma (McNaughton *et al.*, 1991), but at Albert Silver Mine in the south, ages of a disturbance between 400 Ma and 500 Ma were obtained (Robb *et al.*, 1994). These very late isotopic disturbances were not related to mineralising events, but rather to the hydration and oxidation of earlier formed Fe- and Cubearing minerals.

The fluids associated with these major disturbances in radiogenic isotopic systems have been recognised. The fluids trapped in hydrothermal minerals associated with the fracturerelated, replacement-type mineralisation at Albert, Spoedwel and Grass Valley corroborate the hypothesis that circulation of evolving hydrothermal fluids was active from at least 1700 Ma to 400Ma, while the pluton cooled from 600°C to less than 100°C. The fluids associated with Stage 2 (the sulphide assemblage) and Stage 3 (hematite-fluorite assemblage) may be correlated with the disturbances between 1700Ma and 1100Ma, while low temperature (less than 100°C) fluids post-dating the major episodes of mineralisation correlate with the disturbances between 500Ma and 400Ma.

The characteristics of the fluid inclusions, in conjunction with the petrographic, isotopic and geochemical evidence, all point towards fluid mixing as an important mechanism controlling the nature of the granites, as well as the localisation of mineralisation in the eastern lobe of the Bushveld Complex.

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APPENDIX

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
MF1		quartz, biotite, K- feldspar, albite, perthite, zircon		Granophyre, Graphic intergrowths of quartz and hematitised perthite.
MF2	-	quartz, perthite, albite, K-feldspar, blotite		Coarse-grained granophyre.
MF3a		K-feldspar, albite, quartz, sericite, nnuscovite	hematite stringers	White hand specimen. No hematitisation. Muscovite rosettes, sericitic alteration, and hematite parches associated with monazite.
МГЗЬ	0.5-1	quartz, sericite, moscovite, fluorite	chalcopyrite, tetrahedrite/tennantite, sphalerite	White/pale green hand specimen. Intense sericitisation, Dark purple fluorite vein associated with sulphides. Growth zonation observed in fluorite, Fluorite postdates the sulphi %.s.
MF5	>2	quartz, muscovite	pyrite	Large muscovite rosettes.
MF6		chlorite, quartz, albite, perthite, biotite		Granophyre.
MF7a	>2	biotite, chlorite, quartz, ribite, penthite, sericite	hematite, monazite	Medium- to coarse- grained white with dark patches. Perthite is highly albitised. Hematite and biotite occur in dark patches. Albitised hypersolvus granite.

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
MF7b	>2	perthite, quartz, microcline, biotite	? tourmaline	medium- to coarse- grained, albitised perthite with dark retches
MF8				Pale-pink granophyre.
MF9a	.5	perthite, biotite, albite		Pegmatoidal Perthite with biotite patches. Minor albite patches.
МЕЭЬ	05	quartz, perthite, albite (primary and secondary), chlorite, biotite, sericite	hematite	Albitisation of perthite. Feldspars appear zoned. Albite and perthite crystals have secondary growth rims.
MF10	0.5	fluorite, quartz, albite, perthite, K- feldspar, sericite, biotite	monazite, zircon, hematite	Red, fine-grained, porphyritic granite. Interstitial fluorite. Discrete albite grains. Hematitised perthite, as well as discrete fresh K- feldspar. Zircons with 2 visible growth zones. Hematite- fluorite association in blebs.
MF11	>2	quartz, muscovite, perthite, fluorite, muscovite, albate	hematite stringers, monazite	Fusion and albitisation. Interstitial fluorite. Euhedral albite crystals associated with fluorite. Transsolyus granite.
MF12s	0,5	quartz, scricite	monazite	Altered hypersolvus granite with no albite/albitisation. Only muscovitisation.
MF12b	>0.5	quartz, serícite	hematite, monazite	Intense sericitisation, Patch of hematite.

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
MF12c		muscovite, quartz	hematite	Fine-grained, pale green host. Three quartz pulses. Massive quartz and muscovite intergrown. Hematite pseudomorphs after muscovite present.
MF1	0.5	quartz, sericite, perthite, albite, muscovite	· · · · · · · · · · · · · · · · · · ·	Euhedral quartz, Feldspars sericitised, albitised and hematitised. Patches of hematite. No primary grains of albite.
Mf2	1-2	quartz, perthite, albite, sericite, mnscovite, K- feldspar		Sericitisation and albitisation. Multiple quartz phases. Possible introduction of K-feldspar with later quartz pulses.
MF3	0.5-1	quartz, perthite, muscovite, sericite		Muscovite and scricite occur as stringers around quartz and penhite. Cryptocrystalline quartz in patches. No albitisation, Hematite not liberated from perthite lattice.
MF4		quartz, serícite, muscovite rosettes		Intense scricitisation, No feldspars remain, Quartz edges resorbed,
GV01		perthite, quartz, muscovite, chalcedony	hematite	Brecciated, medium-grained red, hypersolvus granite cut by veins filled with 1) chalcedony 2) transparent quartz 3) hematite. Intense hematite of K-fieldspar. No albitisation. Hematite precipitation associated with transparent quartz and postdates chalcedony deposition.

SAMPLE NO.	GANGUE	ORE MINERAL PARAGENETIC	COMMENTS
GV02	quartz, calcite	cassiterite, galena, sphaletite chalcopyrite, chalcocite	Pegmatitic. Euhedral quartz overgrown by milkier quartz and then hematite aggregates. 8 quartz pulses. Calcite is late stage in-fill after milky-limonite-stained quartz. Cassiterite and calcite are intergrown in central portions. Galena, sphalerite, chalcopyrite, postdate early cuhedral quartz.
GV04	quartz, muscovite,	hematite, pyrite, sphalerite	Pegmatoidal quartz associated with muscovite, quartz, hematite and pyrite aggregates.
GV05	quartz vein	hematite	Quartz vein with multiple quartz growth stages. Hosted by medium-grained hematitised granite. quartz 1- white chalecedony quartz 2 - cream chalcedony quartz 3- transparent, small cuhedral crystals quartz 4- transparent, large cuhedral crystals quartz 5- milky, packed with inclusions on the rims. Quartz 6- transparent quartz, cuhedral small quartz 7- milky white with haematite spheroids on crystal surface. Quartz 8- massive in-fill.
GV 0 6	perthite, quartz, muscovite	hematite, goethite	Quartz is interstitial to petthite. Muscovite occurs locally filling entire interstitial cavities. Localized hematite patches.
GV07a	albite	<u> </u>	Granophyre. Hosts quartz vein (GV07b).
GV07b	quatiz		Multiple quartz pulses (>8) . Last pulse capped by hematite.
GV08	quartz, albite, perthite, fluorite, epidote	hematite	Albitisation extensive. Areas near fluorite blebs are more albitised. Fluorite postdates epidote. Hypersolvus granite.
GV09	chalcedony muscovite	hematite	Patchy deer red medium-grained granite. Quartz veinlets. Bleached well rock. No albitisation associated with bleaching. Argillitisation associated with chalcedony. No alteration of wall rock adjacent to chalcedony veins.
GV10	quartz, perthite, muscovite sericite	hematite	Bleached with hematite patches. No primary albite.
GV12	quartz perthite, seticite, albite, muscovite		Hypersolvus granite. Deep red hand specimen. 3 quartz pulses evident.

SECTION ORE MINERAL COMMENTS NC. PARAGENETIC SEOUENCE **RP1.16** pyrite, sphalerite, galena 0.1-0.5mm euhedral/ subhedral pyrite. Disseminated specks (>01mm)magnetite. Massive chlorite, disseminated sulphides. **BPI_17** pyrite, (magnetite) Disseminated pyrite (0 1-0.5mm)- fractured. Small specks of magnetite. Chlorite zone, **RP2.18** magnetite? Small disseminated specks (0.1mm). Granite host (quartz, hematitised feldspar). RP2.25 arsenopyrite, pyrite, Milky-white quartz and smoky-gray quartz. Arsenonyrite sphaleri e, chalcopyrite unfractured, pyrite fractured. Chalcopyrite and sphalerite fill fractures in pyrite. RP2.25 pyrite, galena, sphalerite, quartz with multiple growth stages- bottroidal. chalcopyrite RP2.8A Chlorite zone with guartz yein (milky-white) bearing galena, hematite suiphides. pyrite, hematite. RP3.12c Black with some sulphide specks and quartz cry is. Pyrite (0.2mm) cuhedral/subhe iral, hematite occurs as rosettes. leucoxene, zircon pyrite, galena, bornite. **RP4.9** Hematitised fine-grained granite with milky quartz vein chalcopyrite, hematite, bearing sulphides. Chain of linked enhedral pyrite grains in vein (3mm), Small A15 11c pyrite, hematite disseminated hematite specks in host granite. A18 hematite Massive hematite zone. A30 chalcopyrite, bornite, Bomite altered to chalcocite. Chalconvrite almost totally chalcocite, hematite, replaced. A31 bornite, chalcocite, Well defined paragenesis seen in this section. hematite Á32 hematite Massive hematite cross-cut by quartz veins. Å33 hematite Massive hematite in gangue. hematite, goethite Massive haematite with goethite veinlets. A34 Hematite occurs in rosettes, flakes and anhedral masses. A35 hematite, goethite Goethite veinlets present. AS5.5 hematite Massive hematite. Massive hematite. AS8.5 hematite Needles of hematite project form bottroidal structures. Postdate As15.3 pyrite, tetrahedrite/tennantite. pyrite/chalcopyrite. chalcopyrite, bornite, digenite, hematite Disseminated specks associated with fluorite. AS15.4 bornite, chalcocite, digenite. terrahedrite/tennantite, hematite, fluorite Euhedral pyrite disseminated and as veinlets. Veinlets of arsenopyrite, pyrite, AS17 (10b) chalcopyrite in fractured arsenopyrite. Fine-grained granitic chalcopyrite, hematite, nitchblende host.

TABLE OF POLISHED SECTION DESCRIPTIONS FROM ALBERT SILVER MINE.
TABLE OF POLISHED SECTION DESCRIPTIONS FROM ALBERT SILVER MINE (CONTINUED)

AS17.12a	pyrite, sphalerite, chalcopyrite	Veinlets lined with pyrite and sphalerite, and central portions filled with chalcopyrite.
AS19(16a)	pyrite, arsenopyrite, galena, sphalsrite, chalcopyrite, haematite, magnetite	
AS25 (8h)	pyrite, chalcopyrite, haematite	quartz veins.
AS17.17b	pyrite, arsenopyrite, galena, tetrahedrite/tennantile, chalcopyrite, magnetite	Magnetite and chalcopyrite appear to have precipitated together.

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
A1	≥1	quartz, scricite, cruścovite	hematite, monazite	Quartz in sericite matrix. Hematite associated with muscovite - in stringers.
R53	>1	quartz, sericite, muscovite	monazite, limonite, hematite	As above.
R53 (A5)		quantz, muscovite, sericite	hematite veinlets,	Quartz massive with undulous extinction. Muscovite and sericite along grain boundaries. 2 quartz generations; fine- grained aggregates (0.1mm) filling spaces between coarsor material.
A6	·····	As A5 but more hematite and fracturing of quartz grains.		
А7		quartz	hematite	Quartz fractured and filled by hematite.
A9	>2	albite, nicrocline, biotite, sericite, quartz		Porphyritc granite, Patch parthite, Microsline twinning, Partial hematitisation of feldspar, Biotite interstitial.
AS8.9	0.1-0.3	quartz, sericite, albite, green chlorite, biotite		Hematitised perthite, sericitisation of albite, No frash feldspars.

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
A11	>I	quartz, green/brown chlorite, biotite, nuuscovite, sericite, albite	monazite	Hematitised perthite with white patches (albitisation). Veins filled with sericite cut across patch perthite phenocrysts. Transsolvus granite.
A12	0.1-0.3	quariz, sericite, albite, blotite		Partial sericitisation. Sericitsation occurs in central portions of feldspars, suggesting a secondary episode of feldspar growth.
A13	.2	Sericite, quartz, biotite, muscovite	hematite veinlets	Intense sericitisation of quartz and feldspars.
A14		quartz, muscovite	hematite	Two quartz generations: coarse-grained and cryptocrystalline. Occurs as veins in hematite.
A15	0.3	quariz, sericite, ntuscovite		Two quartz generations,
A17 M78/765	2-5	green chlorite, quartz, muscovite, sericite		Fine-grained green chlorite, Sericite and chlorite intergrown. Extreme alteration.
A18	massive	quartz	bornite, chalcocite, digenite, hematite, sphalerite	Paragenetic sequence uncertain
A19 M78/765	>0.5	quariz, sericite	hematite	Fine-grained, Extreme sericitisation.
A21		quartz, sericite		Quartz highly fractured/shattered.
A23	0.3	quartz, sericite		Fractured quartz with undulous extinction.
A24 M78/765		green chlorite, sericite, muscovite, quartz	pyrite, bornite, chalcocite, hematite, covellite,	Fine-grained. Cryptocrystalline quartz cross-cut by 3 rd quartz generation.
A25	massive	quartz, chalcedony	pyrite, bornite, chalcocite, digenite, hematite	Two quartz generations.
A30		quartz, chalcedony	bornite, chalcocite, magnetite, hematite	Massive hematite zone, Bottroidal growth structures,
A31		quartz	magnetite, hematite	Disseminated.

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
RPIC R53		quartz, sericite, very deep green chlorite, lime-green muscovite	pyrite	Chlorite associated with pyrite. Multiple quartz growth stages marked by fluid inclusions. Disseminated pyrite.
C4 RP1	•	quartz, sericitz, innscovite, green chlorite	pyrite, chalcopyrite, ?sphalerite	Pressibly multiple pyrite growth stages, Chlorite associated with pyrite. Sulphides associated with quartz vein,
RP1d	1	quariz, serícite, ?siderite	hematite needles, chalcopyrite, pyrite veinlets, moluidamum	Feldspar completely sericitised.
· · · ·			veinlets, cassiterite	sulphides, Paragenesis unclear.
RP1f	0.3	quartz, sericite, green chlorite, muscovite		Fe staining in quartz fractures. Chlorite in veinlets.
RP1g	>-0.3	quartz, chlorite sericite,		Abundant sericite.
RPih		quartz, chalcedony	pyrite	Cross-cut by secondary quartz vein.
RP11	0.3	quartz, sericite, muscovile	hematite	Graded contact between hematitised and unhematitised host. Sericite more abundant where less hematite occurs. Corroded quartz.
RP1j		sericite, chlorite, muscovite, quartz		Intergrown. Remnant quartz.
RP1k	<u> </u>	chlorite, sericite, muscovite (blackened)		Chlorite is more abundant than sericite.

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
AS9.1	2-4	perthite, sericite, albite, green chlorite, biotite, fluorite	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Interlocking albite grains, Minor hematitised perthite surrounded by albite.
AS9.2	2-4	quartz, sericite, bíotite	· . · · · · · · · · · · · · · · · · · ·	Sericitised equivalent of AS9.1. No hematitisation.
AS9.4	>0.5	quartz, albite, sericite, K-feldspar, muscovite	hematite, magnetite	Porphyritic. Phenocrysts of quartz and perthite. Hematite rims and stringers occur. Muscovite with black specks (magnetite).
NL1a North Inde	>0,5	quartz, albite, biotite, K-feláspar, zircon, sericite		Fine-grained gray porphyritic granite. Sericitsation of albite. K-feldspar with weak hematite schillers. Subsolvus matrix, Large perthite phenocrysts. Transsolvus granite,
NL1b North lode	>0.5	K-feldspar, albite, quartz, biotite, sericity	hematite	Fine-grained porphyritic granite. Parthite in subsolvus matrix, i.e. transsolvus.
NL1c	0,3-0.5	K-feldspar, albite, quartz, biotite, sericite, zircon	hematite	Fine-grained porphyritic granite. Phenocrysts zoned. Tartan-twinned microcline, Zoned albite with unaltered rim and, sericitised core. Sericitisation of quartz and feldspars. 2 quartz pulses, first embayed, second fresh.

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
NL2		quartz, chalcedony	hematite	Massive hematite ore.
NL3	·	quartz	hematite	Milky-quartz surrounded by bottroidal hematite.
G1	>5	quartz, K-feldspar, biotite, albite,		Coarse-grained granite. Penthite hematitised, albite unhematitised, Albite has secondary growth rims. Central portions sericitised.
Di	>5	chlorite, sericite, quartz	hematite	Completely altered
P1	0.5	chlorite, sericite, quartz, albite,	hanatite	Fine-grained porphyritic granite, sericitised, hematitised and chloritised. Transsolyus granite.
OD1	<u>.</u>	quartz	(chalcopyrite), covellite, hematite	Hematitised breccia, Evidence for hematite/covellite relationship.
OD2		quartz	hematite	Massive hematite vein material.
OD3		quartz, olive-green chlorite,	arsenopyrite, tetrahedrite/tennant ite, chalcopyrite, bornite, chalcocite	Massive ore.
OD4		quartz, chalcedony	tetrahedrite/tennant ite, chalcopyrite, covellite, hematite	Sample banded: chalcopyrite then chalcopyrite /bematite, then hematite.
OD5		quartz	galena, arsenopyrite, hematite	Vein quartz with hematite needles. Galena fills interstitial spaces in quartz.

Appendix

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
W/A	0.5	quartz, albite, biotite, perthite, sericite, K-feldspar, chlorite		Transsolvus granite, Biotite altered to chlorite.
₩/B		perthite,quartz, albite, biotite, sericite, K-feldspar		Medium-grade transsolvus granite grading into fine- grained subsolvus material.
W/C	>5	quartz, biotite, albite, K-feldspar, chlorite		Coarse-grained subsolvus granite.
W2	2	quariz, sericite chlotite	hematite	Medium-grained altered granite with localized patches of hematite. No feldspars remain.
Ϋ3	· · · · · · · · · · ·	quartz, sericite		Medium- to coarse- grained granite. Highly sericitised.
W4	0.5	quartz, chalce.iony, sericite	hematite	Silicified granite. Vein of hematite intergrown with chalcedony.
₩5	0.5	quariz, green chlorite, perthite, zalbite, sericite	hematite	Fine-grained pink granite, High perthite component. Albite and other K- feldspars rare. Hypersolvus granite.
AS13.1	0.3	quartz, green chlorite, sericite, perthite, biotite		Sericitisation of zoned albite (rapakivi?).
A\$13.2		quartz, albite, sericite, chlorite, K-feldspar, biotite, chalcedony	cassiterite?	Fine-grained porphyritic, transsolvus granite. Chlorite veinlets and chloritisation of feldspars. Phenocrysts of patch perthite.

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
AS13.5	0.3	quartz, sericite, green chlorite, perthite	hematite	Highly sericitised, fine- grained granite. Only minor residual perthite remains unsericitised.
AS13.62	0.3	biotite, chlorite, quartz, sericite, K- feldspar, albite, perthite		Biotite altering to chlorite. Fresh K-feldspar partially sericitised.
				perthite and zone albite crystals. Transsolvus granite.
AS25,2	0.5-2	quariz, albite, sericite, Kfeldspar, biotite, chlorite		There appears to be more albite, as secondary
	· · ·			growth and as patches in perthite. Sericitised cores suggest sericitisation
				occurred before albitisation.
AS25.5a	0.3	quartz, sericite, green chlorite		Fine-grained pale green. Quartz and perthite phenocrysts, Intense sericitisation of transsolvus granite
A825.5b	0.3	quartz, sericite, biotite, chlorite	- <u></u>	Fine-grained pale green host. Quartz grains have absorbed boundaries.
AS25.5c	· · · · · · · ·	quartz, sericite, chlorite, muscovite		pale green. Muscovite rosettes.
AS25.6a	0,3	quartz, chlorite, perthite, biotite	hematite	Completely altered,

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEOUENCE	COMMENTS
AS25.6b	0,3	quartz, sericite		Intense sericitisation
A\$25.6c	0.3	quartz, sericite, biotite, chlorite, perthite	· · · · · · · · · · · · · · · · · · ·	Residual patches of hematilised perthite showing the beginnings of sericitisation. Therefore, hematilisation predates sericitisation.
AS25.7	0.3	quariz, scricite, chlorite, muscovite, biotite	· · ·	Biotite replaced by sericite?
AS25.8b	0.3	quartz, chalcedony, sericite, chlorite		Swarm of quartz veins cutting across fine-grained pale- green host. Quartz veins are grouteervstalline
AS25.8g		chalcedony, chlorite	· · · · · · · · · · · ·	<u>, , , , , , , , , , , , , , , , , , , </u>
AS25,9		quartz, scricite, muscovite, chlorite, biotite		Muscovite replaces biotite.
As25. 10f		chalcedony, chlorite	arsenopyrite	arsenopyrite in vein
As25.10g		quartz, green chlorite, inuscovite, sericite	pyrite, arsenopyrite, galena, chalcopyrite	Quartz veins in fine- grained host. Chlorite rosettes surround quartz and suiphides.
AS25.11	0.3	quartz, perthite, sericite, chlorite, albite	<u>_, _ " , · · / " .</u>	Transsolvus granite. Secondary albite present.
AS25.13	0.3-0.5	quartz, sericite, chlorite, biotite	chalcopyrite, hematite	Fine-grained green host. No feldspars left. A patch with biotite, hematite and chalcopyrite. No biotite elsewhere.
AS16.1	0.5	perthite, albite, sericite, quartz, green chlorite	hematite	Pink porphyritic granite. Medium - grained. Discrete feldspars still visible, partially to completely sericitised.

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
AS16.2		quartz, perthite, chlorite, fluorite		Angular perthite and quartz fragments. Fluorite and chlorite, as well as breccia fragments, comented by quartz, Chlorite vein,
A\$16.3A	0,3 (fine)	quartz, K- feldspar, sericite, biotite, chlorite		Sharp boundary hetween fine- and coarse-grained pink granite, Faint
	1 (coarse)	quartz, perthite, albite, scricite, K-feldspar, biotite		hematitisation of perthite. Interlocking crystals. Coarse crystals overgrow border crystals of fine grained material. No erosional boundary. Crystals form interlocking boundary.
As16.4	0.3	quartz, sericite, muscovite, K- feldspar, albite	hematite	K-feldspar is not sericitised.
A\$16.5		quariz, perthite, sericite		Coarse-grained. Sericite occurs along fractures. Chalcedony vein runs parallel to sericite veins.
AS16.62	3-5	albite, quartz, K- feldspær, chlorite, biotite	monazite associated with hiotite	Coarse-grained. Quartz overgrows zoned euhedral albite crystals. Sericitised cores.
AS8.3		quartz	hematite	Massive quartz with hematite veinlets, Multiple quartz growth in bottroidal shape. Hematite lines veins with needles projecting inwards, overgrown by cryptocrystalline quartz and then normal quartz.
A58.7a	0.3	quartz, sericite, muscovite	hematite	Suricitised fine-grained host. Sericite has hematite specks.

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
AS8.4a		quartz	hematitc	Massive quartz. Streaky modulous extinction of quartz grains. Hematite specks rim some early formed eubedral crystals.
AS8.4a		quartz	hematite	As above. Hematite veins cutting through cockscomb quartz with multiple growth stages
AS8.6	0,3	quartz, sericite	hematite	Deep red, patchy, fine- grained material. No feldspars left.
AS8.7	0.3	quariz, sericite, muscovite	hematile	Fine-grained pale green host. Hematite veinlets and rims.
AS8.8	0,3	quartz, sericite, biotite, chlorite	hematite	Fine-grained green host.
AS14.1b		quartz, sericite, muscovite, green chlorite	galena, tetrahedrite /tennantite, sphalerite, chalcopyrite	Fine-grained pale- green host with sulphide specks. Chalcedony veinlets. Sulphide patch associated with massive green chlorite.
AS14.2		quartz, sericite, biotite, chlorite, perthite	hematite, zircon/monazite	Medium-grained porphyritic transsolvus granite.
AS14.3		quariz, sericite, græn chlorîte, biotite, muscovite		Coarse-grained. Biotite altering to chlorite. Quartz veinlets. Muscovite intergrown with chlorite.
AS14.4b		quartz, sericite, green chlorite, chalcedony, muscovite	zircon	Silicification intense.
AS14.5		quartz, sericite, chlorite	sphalerite, hematite	Coarse-grained, pale green host. Sericite and chlorite intergrown.
AS14.7	0.5	quartz, sericite, muscovite	hematite	Fine-grained porphyritic granite, Phenocrysts altered to quartz and sericite.

TABLE OF POLISHED THIN SECTION DESCRIPTIONS FROM UNMINERALISED RED EPISYENITE AT SPOEDWEL.

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
SD58	<2	perthite, zircon, quartz, muscovite, chlorite		Partially fused, hypersolvus granite.
SE04	<2	perthite, albite, quartz, muscovite	bematite	Albitisation of perthite, hematite stringers and rims, partial fusion.
SD59A	2	perthite, zircon, quartz, muscovite	pyrite, chalcopyrite, chalcocite	Hypersolvus granite.
SE01	<2	perthite, albite, zircon, quartz, muscovite, chlorite	chalcopyrite, (Heucoxene)	Partial fusion, hypersolvus granite.
SE02	>2	perthite, nuscovite, chlorite	cassiterite, chalcopyrite	Extreme fusion.
SE03	≥2	perthite, albite, quartz		Albitisation, no fusion, hypersolvus granite.
SD72	≥2	perthite, quartz, chlorite	cassiterite, chalcopyrite	Extreme fusion.
SD31	≥2	perthite, quartz, muscovite, K-feldspar	cassiterite, leucoxene	Transsolvus granite.

Appendix

TABLE OF POLISHED THIN SECTIONS FROM THE SULPHIDE-EPISYENITE CONTACT AT SPGEDWEL.

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
CB06	≥2	perthite, chlorite, K- feldspar, quanz, muscovite, albite	chalcopyrite	Fused transsolvus granite with chalcopyrite veins and albitisation.
SF04	≥2	perthite, muscovite, albite, K-feldspar, quartz	cassiterite, pyrite, chalcopyrite, bornite, covellite	Transsolvus granite,
SC10	≥2	perthite, quartz, chlorite, muscovite	cassiterite, pyrite, chalcopyrite, covellite	Sharp contact, fusion. and albitisation.
P7.01	≥2	perthite, muscovite, K- feldspar, albite, quartz	pyrite, chalcopyrite, chalcocite	Partial fusion, transsolvus, and albitisation.
SF22	≥2	perthite, quartz, muscovite, K-feldspar, sericite	pyrite, chalcopyrite, covellite	Albitised transsolvus granite.
2806	>2	perthite, muscovite, quartz, albite, K- feldspar	arsenopyrite, cassiterite, sphalerite, chalcopyrite, covellite	Transsolvus at hypersolvus-subsolvus granite contact.
SF34	≥2	perthite, K-feldspar, albite, muscovite, quartz	arsenopyrite, cassiterite, sphalerite, chalcopyrite, covellite	Fused traussolvus granite.
SF03	≥2	pesthite, çuartz, albite, sericite, K-feldspar	pyrite, sy halerite, chalcopyrite	Massive chalcopyrite at hypersolvus /subsolvus granite contact. Albitised transsolvus granite.
SF25		perthite, quartz, muscovite, sericite, albite, K-feldspar	arsenopyrite, chalcopyrite	Transsolvus granite.
PP08	≥2	perthite, muscovite, quartz, K-feldspar, albite	pyrite, chalcopyrite, covellite	~anssolvus granite.

TABLE OF POLISHED THIN SECTION DESCRIPTIONS FROM SPOEDWEL WITH DISSEMINATED MINERALISATION.

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
SC06	>>2	perthite, quartz, chlorite, K-feldspar	pyrite, sphalerite, chalcopyrite	Hypersolvus granite with coarse-grained sulphides (>>2mm).
FOP14	≫2	perthite, quariz, chlorite	arsenopyrite, pyrite, cassiterite, sphalerite, chalcopyrite	Extreme fusion of hypersolvus granite with coarse-grained sulphides.
SC04	1	perthite, muscovite, quartz, K-feldspar, albite, fluorifc	pyrite, chalcopyrite	Fused transsolvus granite.
SD61	>>2	perthite, quartz, muscovite,	cassiterite, zircon, pyrite, chalcopyrite, covellite	Partial fusion of hypersolvus granite.
SD04	>>2	perthite, quartz, chlorite, muscovite	pyrite, cassiterite, sphalerite, chalcopyrite, covellite	Fused hypersolvus granite.
SD46	>>2	perthite, quartz, muscovite, fluorite, sericite,	pyrite, chalcopyrite, chalcocite, covellite	Hypersolvus granite.
SD50	≥2	perthite, chlorite (olive-green and grass- green), fluorite, muscovite, sericite	pyrite, chalcopyrite, covellite	chalcopyrite>>pyrite Hypersolvus granite with minor albitisation.
SF26	≥2	perthite, K-feldspar, muscovite, sericite, q	pyrite, chalcopyrite, covellite	Fused hypersolvus granite,
SC02	≥2	nvite, green chlorite, quartz, sericite, albite	cassiterite, sphalerite, chalcopyrite, covellite	Fused hypersolvus granite.
SW21	>2	perthite, quanz, muscovite, sericite	pyrite, chalcopyrite, bornite, chalcocite, covellite	Fused hypersolvus granite. Two veins: 1) muscovite and chalcopyrite 2)quartz
SD62	≥2	perthite, muscovite, albite, green ch' vite	pyrite, cassiterite, chalcopyrite, covellite	Partial fusion. Vein of subsolvus granite in hypersolvus host.
SD64	>>2	perthite, albite, green chlorite, muscovite, quartz, K-feldspar, sericite	pyrite, chalcopyrite	Fusion of transsolvus granite.

TABLE OF POLISHED THIN SECTION DESCRIPTIONS FROM SPOEDWEL WITH DISSEMINATED MINERALISATION (CONTINUED).

SECTION NO.	GRÁIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETI C SEQUENCE	COMMENTS
SD34	»2	perthite, fluorite, quartz, muscovite, K- feldspar, sericite, albite	pyrite, chalcopyrite	Fusion and albitisation at transsolvus-hypersolvus contact.
SW02	>2	perthite, quartz, albite, muscovite, green chlorite	zircon, chalcopyrite	Subsolvus granite.
SD49	>2	perthite, quartz, K- feldspar, muscovite, sericite,	pyrite, chalcopyrite, chalcocite, digenite	Subsolvus material starts crystallizing with pyrite.
SD29B	>1	perthite, green chlorite, monazite, quartz		Very fine-grained, extreme fusion, no albitisation, only hypersolvus material present.
SA06		Perthite, brown chlorite, quartz, muscovite, albite, K- feldspar, sericite	zircon, cassiterite, sphene (leucoxene), pyrite	Disseminated mineralisation at subsolvus/hypersolvus contact. Albitisation of perthite,
SD38	1	perthite, muscovite, albite, K-feldspar, quartz	pyrite, chalcopyrite, covellite	Albitisation of fused perthite, minor subsolvus granite and disseminated sulphides.
SA01	>1	quartz, muscovite, sericite, albite, K- feldspar,	monazite, cassiterite, lencoxene, chalcopyrite, covellite	Partial albitisation, and extreme fusion of host. Disseminated chalcopyrite. Sericitisation near contact with subsolvus granite.
SA09	≥1	sericite, fluorite, muscovite, brown chlorite	cassiterite, pyrite, chalcopyrite, boraite, chalcocite, covellite	Fine-grained subsolvus granite.
PP03	1	perthite, albite (X2), sericite, muscovite	goethite, chalcopyrite, covellite	Extreme fusion and albitisation.
SD59B	>1	muscovite, quartz, green chlorite associated with quartz vein	goethite, chalcopyrite, bornite, chalcocite	Fusion, local albitisation, and silicification associated with quartz vein.
SE05	1	perthite, quartz, K- feldspar, muscovite, fluorite, albite (X2), sericite	cassiterite, hematite,	Albitisation of perthite in transsolvus granite. Subsolvus material associated with fluorite and sulphides.

TABLE OF POLISHED THIN SECTION DESCRIPTIONS FROM THE MASSIVE SULPHIDE ZONE AT SPOEDWEL.

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEOUENCE	COMMENTS
SP23		albite, K-feldspar, quartz, muscovite,	massive pyrite, sphalerite, chalcopyrite	No perthite, Subsolvus granite.
SF24		muscovite, albite, K- feldspar	huge pyrite grains, chalcopyrite massive	Subsolvus material embayed by sulphides.
SF08	· . •	albite, muscovite, quartz, K-fèldspar	arsenopyrite, chalcopyrite, galena, tetrahedrite/tennantite, sphalerite	Sphalerite surrounds pyrite and chalcopyrite. Predominantly albite matrix. Note chalcopyrite precedes galeng and sphalerite.
CB50		perthite, albite, muscovite, sericite, K- feldspar	monazite, arsenopyrite, pyrite, sphalerite, chalcopyrite	Pyrite overgrowth on albitised perthite grains.
SF20		perthite, quartz, sericite, muscovite, albite, K-feldspar	pyrite, chalcopyrite, covellite	Small perthite specks in subsolvas matrix.
CB11		K-feldspar., quartz, aibite, muscovite, scricite	arsenopyrite, pyrite, chalcopyrite	Albite, K-feldspar, and quartz of subsolvus material fotati within pyrite grains.
SF05		quartz, albite, muscovite, K-feldspar	pyrite, chalcopyrite	Massive sulphide, minor gangue component.
\$12*		quartz, sericite	pyrite, chalcopyrite, covellite	Massive chalcopyrite. No feldspars present.
PB20		quartz, muscovite,	cassiterite, monazite, pyrite, chalcopyrite, covellite,	Large pyrite grains surrounded by massive chalcopyrite. Large crystals of monazite.
SF25B		(perthite), muscovite, aïbite, quastz, K- feldspar	pyrite, chalcopyrite, covellite, monazite	Transsolvus granite,
SD43		quartz, muscovite, albite, scricite, K- feldspar	pyrite, chalcopyrite, zircon	Subsolvus granite.
SD45A	>2	Chlorite, quartz	pyrite, chalcopyrite	Pyrite and chaicopyrite in chlorite matrix. Quartz embayed by chlorite.
SF28	>2	K-feldspar, quartz, muscovite, albite	arsenopyrite, pyrite, chalcopyrite, covellite	Subsolvus matrix.

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TABLE OF POLISHED THIN SECTION DESCRIPTIONS FROM THE MASSIVE SULPHIDE ZONE AT SPOEDWEL (CONTINUED).

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
SD63	>2	quartz, muscovite, albite, K-feldspar, green chlorite	pyrite, chalcopyrite, covellite	Subsolvas matrix.
SD09	1	albite, K-feldspar, quartz, muscovite	cassiterite, pyrite, chalcopyrite, covellite	Subsolvus matrix.
SD25		quartz, muscovite, albite, K-feldspar, green chlorite	chalcopyrite, covellite	Subsolvus matrix.
SD49B	1	green chlorite, quartz	pyrite, chalcopyrite, covellite, zircon	Chlorite matrix.
PB02		albite, quartz, muscovite, fluorite, sericite, residual perthite, green chlorite, (K-feldspar)	Arsenopyrite, galena, chalcopyrite, covellite magnetite	Well zoned quartz inside chalcopyrite masses. Albits highly sericitised. Fluorite precipitation occurred before chalcopyrite.
· · ·				Veins of magnetite lined by covellite within chat opyrite.
SD26		perthite, muscovite, albite, green chlorite, quartz, sericite, K- feldspar	pyrite, chalcopyrite, covellite	Pronounced albitisation of perthite.
SW01		Green chlorite, albite, muscovite, sericite, quartz, K-feldspar	leucoxene, pyrite, arsenopyrite, chalcopyrite, monazite, covellite	Subsolvus granite.
SF30		quartz, albite, muscovite, sericite, K- feldspar, green chlorite	zircon, pyrite, galena, sphalerite	Albite is sericitised and chloritised. Subsolvus granite.
SD45B	>2	green chlorite, quartz	zircon pyrite, chalcupyrite,	Chlorite matrix containing zircons with alteration haloes.
SD45A	2	green chlorite, quartz	pyrite, chalcopyrite	Chlorite matrix,
SF36	>1	albite, quartz, K- feldspar, muscovite, green chlorite	pyrite, galena, sphalerite	Subsolvus granite.
SF33	>1	albite, quartz, K feldspar, muscovite,	pyrite, galena, chalcopyrite, sphalerite	Subsolvus granite. Questionable paragenesis.

TABLE OF POLISHED THIN SECTION DESCRIPTIONS FROM THE MASSIVE SULPHIDE ZONE AT SPOEDWEL (CONTINUED).

SECTION NO	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
SF31	>1	albite, quartz, K-felospar, muscovite, green chlorite	galena, sphalerite only	Subsolvus granite.
SD55A		quartz veinlets, chlorite	pvrite, sphalerite, magnetite	Chlorite matrix. Vugs lined by small quartz crystals. Magnetite in veins.
SD70		green chlorite, quartz,	chalcopyrite, chalcocite, bornite, magnetite? Limonite, zircon	Chlorite matrix with quartz veins and vugs. Quartz is coarse- grained in vugs and fine-grained in veins.
SD73	>2	sericite, muscovite, green chlorite, K-feldspar, albite	pyrite only	Extreme sericitisation of original subsolvus host.
SD27	··· · · · · · · · · · · · · · · · · ·	quariz, green chlorite, very fine grained quariz (chaledony?), sericite	pyrite, sphalerite, chalcocite, chalcocite, chalcopyrite, covellite, magnetite	Questionable paragenesis. Chlorite matrix.
WS01		green chlorite, quartz	chalcopyrite veinlets, bornite veinlets in chalcopyrite veinlets, chalcocite rims on chalcocite rims on chalcopyrite, monazite in quartz veins, zircon	Chlorite matrix, Euhedral perthite crystal outlines still visible.

TABLE OF POLISHED THIN SECTION DESCRIPTION OF MISCELLANEOUS SAMPLES FROM SPOEDWEL.

SECTION NO.	GRAIN SIZE (MM)	GANGUE MINERALS	ORE MINERAL PARAGENETIC SEQUENCE	COMMENTS
FG01	0,1-0,5	(perthite?), quartz, green chlorite, albite, biotite		Small scale graphic intergrowths. Granophyric texture.
FG03	0.5-1	biotite, albite, haematised feldspar (K-feldspar)	zircon	As above.
5005	>>2	perihite, green chlorite, quartz	monazite, pyrite, chalcopyrite	Transition between heavily and partially chloritised hypersolvus material.
SC09	2	perthite, green chlorite, sericite, quartz	monazite, pyrite, chalcopyrite, bornite, chalcocite	Fused hypersolvus granite.
SC08	·	perthite, muscovite, quartz, green chlorite, albite	zircon, pyrite, sphalerite, chalcopyrite	Massive muscovite zone at contact between fused hypersolvus material and subsolvus material,
SD71		perthite, quartz, green chlorite	monazite only	Massive quartz invasion of chlorite matrix.
SF38		albite, green chlorite, muscovite, quartz, K- feldspar	pyrite, galena only	Chloritised subsolvus granite.



FIGURE 27b strike & dip of joint/fracture planes 045/22 Strike & dip of lithological contact oochi Strike & dip of shear/shear zane 7777 Coarse-grained Klipkloof granite 1000 Altitised Kiipkloof granite with Observed lithological contacts Interred lithological contacts 223 Porphyritic Klipkioof granite Klipkloof granite METRES 500 Rivers/atreama <u>⁺ †</u> Nebo gronite LEGEND Dirt roads Tar roads / V Dolerite Fault ì 7 24 54'S 24'55'5 ± 24-57'S 24'56'S 29'30'E 29,30 RDENZOEK 29*29'E 29'29' ELEGEN 756 25'28' 29"28E 29'27' 29°27*E 24'57'S [24 55 S 24'55'S 2454'5







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Figure 5.42 A) Synthetic NaCl fluid inclusion B) Synthetic KCl fluid inclusion





1.7















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Magnification: X200













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SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	Intermediat	e meltini	g events	T final melting	Th Th	1 CO2	Tfinal melting CO2
GV01	TRAIL A	S	-38,5	1				-5.5	1		
FIELD 1	B	S		[-4.7			
	TRAIL A	S	-47	-41				2			
	В	S	-47					-5.1			
	TRAIL (X20)	S	-42					2.1			
	A	S	-36					-1.5			
<u>,</u>	B	S	-43	1				-1.5			
<u>;</u> ,	CO2 TRAIL 1	S		<u> </u>	[27.7	-57.4
		S								28,3	-57.4
		S								22.5	-57.4
		S								23.1	-57.4
· · · · · · · · · · · · · · · · · · ·	CO2 TRAIL 2	S					· · · -			22.8	-57.4
		S								26.8	-57.4
		S								27.8	-57.4
		S						9		27.7	-57.4
		S								26,5	-57.4
· · · · · · · · · · · · · · · · · · ·		Ş		1						23.1	-57.4
FIELD 2	CO2 TRAIL 3 A	S								24.9	-57.4
	B	S								[.] 27,4	-57.4
	CO2 TRAIL 3 A	S	1							27.3	-57.4
	D	S	-97.9							26,2	-57.4
	E	S								26.2	-57.4
	F	S								26.7	-57.4
	G	S	;	1						26.7	-57.4
	CO2 TRAIL 4 H	Ş								26.2	-57.4
FIELD 3	CO2 TRAIL 1	S	-96.4	í						25.9	-57.8
	2	S	-98.9							25.3	-57.8
	3	S	Ì	1				· · · · ·	·	25.3	-57.8
	4	S		<u> </u>						24.7	-57.8
	5	S		l						25.4	-57.8
	6	<u> </u>		-53	-48	-35	-10.1			25.2	-57.8 G
	TRAIL A	S	<u> </u>				<u> </u>	16.1			-57.8
	B	S		1				16,1			55
	M		-96.4					1		26.1	-57.6 🍒
·	C			1				-1			le le

Chapter 5 - Microthermometry

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	Intermedia	te meltin	g events	l' final melting	Th	Th CO2	Tfinal melting CO2
	D				· · ·			0			
GV02	A		-80.2	-48	-38	-22.3			141		
FIELD 1	B		-71							Í	
	C		-71								
	D		-71								
	E		-71								
	F		-71	·	· · · ·						
	G		-59.5						152	۱	
	Н		-54					-16.9	149		
	l		-54				··· ·	-16,9	160		
	A	S	-P';	-46	-36	-23.9		-7.7			
	B	S	-44.6					-15.1	L		
<u></u>	C	S	-74					-7			
	E	S	-48					-14.9	<u> </u>		
								L			
	TRAILA	S	-66	-50	39	-23		-14	133		
	В	S	-64			· · · · ·		-14	134	ļ	
	C	S	-64					-14	ļ	ļ.,	
	TRAIL D	<u> </u>	-80	-52	31	-22.5		-6.8	<u> </u>		
	ZONE 1 A	P	-35						143		
	C	P	-49	-44	-19			<u> </u>	167		
	D D	P	-36					4	143		
	E	P	-45	-	<u> </u>		•	-2.4	134		
	ZONE 2 (X50)	P	-46	-43				-0.4	194		
	CO2 TRAIL A	S	-93	 			· · · · · · · · · · · · · · · · · · ·		L	29.9	-57,4
	(X20)B	S	-92		· ····					29.9	-57.4
	D	5	<u> </u>	[· · · ·		[29.9	-57.4
	E		-96	L				7.5	>205		
QUARTZ 3		····	ļ					<u> </u>		<u> </u>	
	A	P	ļ	Ĺ			· . 	· · · · · · · · · · · · · · · · · · ·	 	29.9	-57.4
	В	P	L	-50	-37	-27	24				····
	C	P		-50	-37	-27	24	-9.5			
	D	P						L		29.2	
	ZONE (X100)	P	-34	i				-0.7			

Chapter 5 - Microthermometry

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	Intermedia	te melting	g events	T final melting	Th	Th CO2	Tfinal melting CO2
	ZONE 1A	P	· · ·					-4			
	B	P						1	233		
	E	P						-5,5		l	
	F	P						-6.7	214		
	G	P					····	-0.5	217		
	D	P						0.4	ſ		
GV04	A	S	-35.2	-33	-23			-1.5	108		
FIELD 1	5	S	-35,2	33	-23			-2.1	127		
	C	S	-35.2	-33	-23			-2.1	127		
	A	8	-38.7	-33	-23			-1	99		
	B	S	-35.7	-33	-23			-1			
	D	S		-33	-23			0.6	<u> </u>		
	X	<u> </u>	-39,9	-33	-23	·	······	-1.7	99		
	B	<u> </u>	-40	-33	-23			-2.8	128		
	C C	S	-39	-33	-23			-1.5	83		
0.05	000 7040 040			ļ			·		<u> </u>	474	E7 4
	CO2 TRAIL (A15)	°	-90	<u> </u>					<u> </u>	21.1	-57.4
	LOOZ TRAIL (ATS)		-90	}				101	}	20.4	-57.4
FLOORITE				-45	-36	· · · · · ·		3		24.0	-57.7
		<u> </u>	-52	-45	-36			-0.0	·		
			-02	-45	-36			-4.3	· · · · ·	<u> </u>	
	<u> </u>	<u>S</u>	-44	-33	-22			-14.9	·		· · · · · · · · · · · · · · · · · · ·
·····				<u> </u>						h	······································
FIELD 1	CO2 TRAIL A	S	-96					7.3	1	30	-57.1
QUARTZ	CO2 TRAIL B	S	-95							28.4	
	C C	P	-42		-38			-17			
	D	P	-42			-24		-5			
	E	P						-4			
	ZONE (X100)	P	-40	-37				-17			
VEIN QUARTZ											
FIELD 1	D	P	-49	-27				-7.9	101		
QUARTZ 4	E	P	-46						101		
	F		-52					-6.8	101		

Chapter 5 - Microthermometry Grass Valley

									•		
	• •										
SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	Intermedia	te meltin	g events	T final melting	Th	Th CO2	Tfinal melting CO2
	A		-46]	-8,7	101		
	B		-45			· ·	f	-8.6	101		•
	C		·			•		-7.3	101	1	· · · · · · · · · · · · · · · · · · ·
FIELD 2		· · · · · · · · · · · · · · · · · · ·					· ·		<u> </u>		
QUARTZ 8,7 & 8	A		-95.3					· ·		29.8	-57
	C								1	30	-:7
CHIP 3								· · · ·			
QUARTZ 7	A	P		1					T	27.4	
	B	P	-44	-39				-7			
	C	P						-7	146		
	D	P		[-7	<u>' </u>		
	E	P						-1.5	195		
	F	P						-6.5	1		
GV06			<u> </u>						1		
FIELD 2 (1)	CO2 TRAIL A	S					[29.3	······································
	B	S								28,3	
· · · · · · · · · · · · · · · · · · ·	C	S		· ·						28,9	
	D	Ś	-95.9	r——				8.4	>200	28,4	-57.4
FIELD 2 (2)	ZONE (X30)	P	-45	-35.6				-22.9	175		
		P						-19.7			
· · · · · · · · · · · · · · · · · · ·	(X8)	P	-52.9	-39	-33			-15.3	113		
GV10	A	-53	-49	-42	22	·	<u> </u>	-17	157		·····
	C	-,			· · · · · · · · · · · · · · · · · · ·	·	ţ		<u> </u>	25.3	
	D			· · ·			1	-18	1		·····
	Ē	-55		1			<u> </u>		1	180	······································
	F		· · · · ·	1	· · · · · · · · · · · · · · · · · · ·		<u> </u>	-1.1	1		
	1.2.3	P	i — —	-34.6	-30	-,25	<u> </u>	13.2	1	1	······································

Chapter 5 - Microthermometry Grass Valley

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	INTERME	DIATE MEL	TING EVE	Tfinal melting	Th	ThCO2
SP3	1	P	-46		-36			0.8	n/a	
fiuorite	2	Р	-46		-36		[]	-12	n/a	
· · · · · · · · · · · · · · · · · · ·	3	<u> </u>	-46		-36			-4.6	187	
	4	P	-48		-36			?	180	
	X		-52		_37	-23	-15	-13.7	?	
	Y	<u> </u>	-59		-33	-16		-12	190	
	A			-46					205	
	B	P		-42		· · ·			259	
SP3(.)	X11	S	-42					-0.5	114	
fluorite				· · · · · · · · · · · · · · · · · · ·				-0.5	270	
······································								-0.5	237	
]]							-0.5	243	
						· ·		-0.5	255	
SP3	X10	S	-55	-44	-37	-30	-15,9	-8.6	123	
			-59	-44	-37	-30	-15.9	-9.5	124	
			-48	-44	-37	-30	-15.9	-8.7	128	
SP3	X6	S	-40	-37				-0.6	n/a	
SP3	A (X250)	?	-61.5	-42				<u>-</u> 13.2	128	
	B		-61.5	-42			1 1	-13	127	
	C		-61.5	-42				-13.1	128	
			[-65;-54]	42				-13.2	[137;150]	
SP3	X100	P	-49	-40	-23.8	-19	-6.9	-4.3	150	
SP3	6							-4.7		
	5							-1.2		
	2							-0.4		·····
	B							-3.8		
	N		-42					-2.9		
			-79.1	-47	-43	-20			146	
SP3	X200	?	-43		-20			-1.2	129	
SP3								-0.2	220	
	A	P	-37	-40				-3.1	[189:205]	
	В	P	-49	-40				-4.6	[189;205]	
	C	P	-49	-40				-13.2	[189;205]	
	D	P	?					-3	?	•
	C	P	-51					-4.5	147	
	D	P	-51					?	230	

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	INTERMED	DIATE MEL	TING EVE	Tfinal melting	Th	ThCO2
SP3	1		-45	-36				-8.4		
	2		-38		-23			-4.3		
	3		-43		-23			-4.3		
SP3	X50	S	-49	-35				[-3.9;-2.5]	[174;220]	
SP2(1)		P	-69	-43.5			L <u></u>	-27	167.5	
	1 TO 8	P	-67	-35				-23	184	
SP2(1)	1,2,3	P	-59					-34	22.8	
SP2(1)	3	<u></u>	-57	-44		i 				
8P2(1)	4		-56.3	-50		<u></u>	l	-27		
SP2(1)	A	P							147	L
	B	P		-45	-32.9		· · · · · · · · · · · · · · · · · · ·	[-19;-23]	191	
	C	P	-57	-47	-32.9			[-19;-23]		
	D	P	-51.9	-45	-32.9	-28		[-19;-23]		·
	E	P	-57	-47				-19,9	216	
SP2(1)		P	-83	-40				-11.9		
		P	-57	-40			{	-22.7		
		P	-53	-42				-26	143	
	· · · · ·	PS	-65	-47				-23	161	
		PS	-63	-47				-23	156	
		PS	-70	-47				-23		
SP2(4)	A	P	-72	-53	-44	-35		D.1	164	
	B	P	-46			-22		-10.2	240	
	C	P	-51			-22		-6.2	175	
	D	P	-72			-44	┝┅╍╍┉┝		125	
	E	P	-89	-67		-49	-38	7-38	164	
	A	S	-44	-53	······	-35	-6,9	-6.9	106	
	B)	S	-44			· · ·	!	0		
·····	1	P	-72.8	·				-10.1		
	2	P	-74.4		·				* * *	
SP1	A	P		-52	-47	-31,7	[3	181	
	B	P	-83	-58		<u> </u>	1	-34	155	
	Ĉl	P	-77					-31	155	
1		S	-83	-54			h	1	173	
	4	S	-77				<u>¦ · - · - </u> †		159	
	51	P	-81	-52			r 	-30	149	

Chapter 5 - Microthermometry Spoedwel

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	INTERMEDIATE MEL	TING EVE	Tfinal melting	Th	ThCO2
	6	P					-28	173	
SP2(3)			-42	>-48			-7.4		
QZ							0		
			-42				0		
			-39				3		
	<u> </u>		-39				10		
			42.4				-9		
			-42.4				-4.1		
<u></u>		· ····································	-64	>-36			-4.1		
	X6	···	-64				-17.2		
SP2(3)	1	P	-48	-39	[0		
·····	2	P	-48	-39			0		
	3	P	-46	49			0	·	
	4	P	-29		}		-2		
	5	P	······································	_ <u> </u>		{	-4		
	X100	5			{	hl	[0;3]		
· · · · · · · · · · · · · · · · · · ·	<u>X0</u>	8	88-		<u> </u>	<u> </u>	-38	93	
	5	3	-39	<u>.</u>	<u> </u>		1.7	111.5	
t 4	<u>۲</u>	3	-31.1		{		1,0	138	
	<u>د بر ا</u>	0	<u>`</u> `	f	<u> </u>				
,,,,,,	<u>'</u>			30	<u> </u>	<u>}</u>			······
••				<u>פניי</u> כ	<u>├</u>		0.3		
			-40		<u> </u>	<u> </u>	0.0		
······	4,5	20	-40	<u> </u>	· · · · · · · · · · · · · · · · · · ·				
		70	71		<u>╎</u> ─────┤╍ <i>───</i> ─┤	}	v,5		
		20			┟╌╌╌╌╌╌╎┈╴╌┈╴╴				
	4	20	-71	-50			-14 4		
SP7 (ii)	1	P	-40	<-28	<u>├</u>	<u> </u>		225	······
	2	P	-40	<-28	<u></u>	<u></u>	-5	206	
	3	P	-40	<-28	<u> </u>	[-5	206	·
·····		Р	-40	<-28	<u>├</u>	[-5	190	
i	5	P	-40	<-28			-5		
	A	PS	-52	<-23	/────		0	288	
	C	PS	-52	<-23				272	
					<u></u>				

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	INTERME	DIATE MEL	TING EVE	Tfinal melting	Th	ThCO2
SP7 (I)	b	P	-52					-5.1	228	
	X									
	1		-52							·
	2			-34						
	3			-34						
	4			-34				-7.9	173	
	5								190	
	7							-9,8	228	
SP7 (2)	A		-85						·	
	B		-85	-52.2						
	C		-85	-52.2						
	D		-85							
· · · · · · · · · · · · · · · · · · ·	A	\$	-39					-3.6	86	
	B	S	-49	l				-3.6	197	
	X						_ <u></u>		125	
	Y								219	
	<u>Z</u>	P			ļ	·	ļ	·	174	
<u>L1</u>	1	P	44		-30	· · · · · · · · · · · · · · · · · · ·	<u> </u>			
	2,3	P	-44		-23			-5.5	216	
·····	4	P	-44	 		<u> </u>	[]	-10.4	200	
·	1		-51	-35	· ·			-4,9	200	
	2	······	·			L		-5,6	219	
	1			-30,1	-20	<u> </u>		-5,6	219	
	2							-4.1	216	
	3	P	-54	-35	-21			-6,5	162	
	4	P	-49	-35	-29	-9.1		-6,5	146	
······································	5	PS			<u></u>				182	
	6	PS		L					182	
	7	PS							182	
<u>SP7(I)</u>	A	S	·	-44	-21			-9.9		
	1	S	-47	-44	-31		}	-10.2		
****	2	<u> </u>	Ĺ	-52		<u> </u>	i	-0.9		
·]		<u> </u>		!			
		·	[
			ļ							
		_			Į .	<u> </u>	L /			Ì

· .							1. A.			
						2 ×		· · · · · ·		
SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	INTERMED	DIATE MEL	TING EVEL	Tfinal melting	Th	ThCO2
SP2	N		-57	-39	-33			-13.8		
	A	P	-79	[-33				170	
····	B	P	-79	-39				-0.8		
······································	C	P	-79	1	-29			-0,8	******	
	D	P	-65	{				-33	178	
}	X		-31	-24			1	-22	378.5	
	Y		-87	{				-31	255.8	
	N		-83						310	
1	Z		-76						240	
	1		-76	1				0		
	2		-76							
.1	A	P	-35	-29	-17.8			0.2	193	
	B	P	-35	-29				0.2	193	
	1		-35	-29				0.3	<205	
	2		-35	-29				0.3	<205	
	3		-35	-29				0.3	187	
	<u>A</u>		-42	-22	-29.4			0,3	179	
	X		-32		·			0.3	160	
	Ð		-32	-17				0.3		
	1	P	-43					0.3	174	
	2	P	-43					-4.9	194	
	3	S	-43					-4.9	189.6	
	1								213	
	2		-42.4					0.3	191	
	1	P	-50	<-29				0.3	214	
	2	P	-50	<-29				-5	244	
	3								203	
	4								220	
SP2	4		-76	-39	-31	-10		5.7		· · · · · · · · · · · · · · · · · · ·
	1	P	-87	-45	-35	-30		5.6	128	
	A	P	-65	-30,3				-14.1	220	
	<u> </u>	<u>P</u>	-65	-30,3				-15.8	220	
	C	P	-74	-38	-28	-22		-9	217	
<u></u>	A	<u> </u>	-71		-24	-18		-18		
	B	P	-58	ļ	-23.4	I <u></u>			232	
	<u> </u>	P	-65	l	-29.7	-22,1	1	-12.8	222	

SAMPLE NO.	INCLUSION	ORIGIN	Tireeze	Te	INTERME	DIATE MEL	TING EVE	Tfinal melting	Th	ThCO2
SP2	1,2,3	S	-64	-30.3	-24	-9				
	A		-67	-45	-38	-29		9,4		
	Bį		-59	-38.8	-28	-23		7.6		
	C		-63	-38	-24	-21.5		10.2		
·····	A		-57	-39	-33	-23.3				
	N			-27	-16.6			-13,8		
	A	<u></u>	-65	-39	-33	-23.9			·······	,,,,,,
	B		-65	-39		-23.9		-0.8		
	C	···· — _ · · · = _ · · ·	-65	-39	-29	-23.9		-0.8		· · · · · · · · · · · · · · · · · · ·
SP3	A	P	-56.7	-39	-28	-11		-4,5	un	
· · · · · · · · · · · · · · · · · · ·	В	P	-56.7	-39	-28	-24		-9.3		
	C	P	-56	-39				-9,9		
	1	P	-56	-39				-8.7		
	2	P	-56	-39				-8.4		
	3	P	-59	-39				-8.4		
	A	P	-52	-30	-21	-12.2		-7.3	152	
	B	P	-52	-34	-21			-7.8	163	
	C	P	-52	-34	-21			-5.8		
	D	P	-52	-34	-21			-2.2		
	E	P	-52	-34	-21			-2.8		
	X	S	-70	-53	-43	-33		-16	149	
	A	S	-64	-53	-43	-33		-16	123	
	В	S	-67	-53	-43	-33		-16.2	136	
	C	P	-48	-41		-30.3		-1	149.8	
	D	P	-48	-41	-30.5	-13		-1	136	
	E	P			-30.5	-13		-1	158	
	F	P						-1	168	·····
	Ý	P						· · · · · · · · · · · · · · · · · · ·	409	
SP3 (III)	1 (X32)	P	-53	-40				-10		
	2	P	-48	-38				-9	97	
	3	P	-87	-43						
	A		-46	-21				-9.2	158	
	B		-42					0.1		
	C		-42					0.1		······································
	5	S	-59	-30	-21			-10		

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	INTERMEDIA	TE MELTING	EVENTS	Tfinal melting	Th	ThCO2
GC600	A	S	-67	-51	-35	-24		-3.7	165	·
CHIP 1	B	S		-48	-35	-24		1.7	200.9	
	D{	S	-68	-50	-37				165	
	E	S	-64						165	
	X	9	-38	-29				-1.2	200	·
CHIP 2	A	٩	-45	-36	-12.8			-2.7	186	
	Б,C,D	Р		}				· · · · · · · · · · · · · · · · · · ·	176	
	E	P	-67	-47	-28			9	163.8	
CHIP 3	1								164	
	2			1					163.2	
	A		-40					-3.9		
	8		-40					-3.9		
	N								162	
	A		-59	·				?-40		
	8		-59					7-41		
	A	•	-48	-34	-24			-22.2		
	B,C		-48	-34	-24	· · · · ·		-22.2		
CHIP 2C	C		-71	59				-37.9		
	A		-71	-59	-27	-16	-3	4.3		
	D		-71	-59						
	B		-71	-59		· · · ·		-38		
	1,2,3		-69	-50		· · · · · · · · · · · · · · · · · · ·		-26]	
	A,B,		-69	-50	{	·····		-24.2		
	B		-83	-51	-35	-5.9		3	142	
	A		-65	-51	-35	-25	-7,6	2.2	142	
									}	
						·····				
]									*****	
						· · ·				
					:				ĺ	
	}									
		· · · · · · · · · · · · · · · · · · ·								
	1									

Appendix

Chapter 5 - Microthermometry Dronkfontein

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	INTERMEDIA	TE MELTING	EVENTS	Tfinal melting	Th	ThCO2
CHIP 2D	1,2,3	S	-59					-29	155	
	X,Y,Z	S						-37.9	128	
	1,2	S			· · · · · · · · · · · · · · · · · · ·			5		
	Z	S						-33.3		
	A	P	-72	-54	-24.6			6	126	
	B{	P	-72	-54	-24.6			0.1	126	
	C	P	-72	-54	-24.6			-12.3	127	
	C	P	-72	-54	-24.6					
	D,E	P	-72	-54	-24.6					
	1,2,3,4	S	-78	-54	-33			-25.9	123	
	5	S	-63.4	-50				6	142	
	A,	S	-78	-50.9	-26.8			-26.8	165	
	B	S							165	
	1	P							235	
	2	P			-33	-1.1		-1.1	276	
	3	P							75	
	4	9						-1	231	
r	A,B,C	P	1	-45	-30,	-20.8			164	
GC40L	N,A,B	8		i				?-46	98	
	C,X	S		-52				-42	98	
	M	S	-88					-42	125	
	X	S						-42		
	A	5	-59.5	-43	-35	-22	-12.3	-5,3	<100	
	TRAIL (X250)	S	-54					-3,3	<101	
	1,2	S	-54					-4.7	<102	
	<u> </u>	S	-54					-8	<103	
	4	S	-54					-2.2	<104	
	A,B	P	-71	; <u>3</u>				?		
	C	P	-71	- 33				?		
	D D	P	-71	-53				?		
	E	P	-71	-53				?		î
	F	P	-71	-53	{			-42		
	G	P	-71	-53				-34	116	
	H	P	-71	-53					135	
	۱ I	P	-71	-53					140	

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SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	INTERMEDL	ATE MELTING EVENT	S Tfinal melting	Th	ThCO2
ZNS	ZONE 1	P	-47	-39.1	-27		-12	188	
SPHALERITE	ZONE 2	P	-50	-32		· · · · · · · · · · · · · · · · · · ·	-10	200-215	
SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	INTERMEDL	ATE MELTING EVENT	S Tfinal melting	Th	ThCO2
HBQ	A	P	-52	-31	-22		-10.4	206.1	
QUARTZ	B	P	-33	-21	-6,4		0.1	201.6	
	X	P						172	
	A	P	-62	-43	-38		-2.4	212	
	В	P	-33	-37	-34		-1.6	198	
	С	P	-33	-37				208	
	D	P	-33	-37	-34		-1.6	212	
	E	P	-33	-37	-34		-21	212	
	F	P	-33	-43	-34		-7.9	204	
HBQ (2)	1			-30			2,2		
	2			-30			-20.5	132	
	3			-30			-20,5		
	4			-30			-22		
	5			-30			-21		
	6			-30			-7.3		
	X			-30			-11	207	
	1						0.1	97.5	
	2							218	
	3							149	
	4						-15	137	
	5	·	-45	-35			-21.5	137	
	7		-46	35			0,1	218	
	<u> </u>		-48	-46	Ĺ		-3.7	244	
	В		-48	-29			-22.4		
	Ć,D		-48					248	
	1		-62	·····	<u> </u>		-16.9		
	2		-62				-15.1	195	
	3		-62	-45				243	
	4		-69	-40			-21.6		
	5	1	-69		1		-20.6		

	. ·					•				
SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	INTERMED!	ATE MELTIN	G EVENTS	Tfinal melting	Th	ThCO2
HB1 (4)	TRAIL (X25)	S						1	221-225	
	TRAIL (X25)	S							246.5	
	A	S						1	233	
	TRAIL (X.100)	S						-8.1	205	
	B	S						-7	212	
	TRAIL (X5)	8						-7.9	227	
	A	S		-48	-24.5			-1.9	231.1	
	B	S	-73				·	-19.1	151	
	Ç	S	-73	1				-19.1	151	_
	X (X 2)	S						-0.4	207	
	TRAIL (X200)	S	-56	-43	-31	-20		-6.4		
	A	S	-46					-2.1	208	
	B	S	-52					-7.9	191	
	C	S	-52					-5.5	154	
	D,E	S						-8.2	204	
	TRAIL(X50)	S						-8	224	
HB1 (5)	TRAIL (X4)	S							168	
	TRAIL (X3)	8					[214	
	A	5					} 		184	
	TRAIL (X50)	S					[{	210	
	A	S							236	
	B	S							183	
	C	S							183	
	D,E	S							231	
	TRAIL (X20)	S							203-216	
	TRAIL (X10)	s							215	
	TRAIL (X25)	S[165	
	A	·		{				-1.6	186	
	<u> </u>							0	165	······································
								-1.5	165	
·······	D	f						-0.5	189	• - <i></i>
	E					<u> </u>	ļ	-0.4	197	
	F							0.4		
							ļ,	- <u> </u>		
			1					1		

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Те	INTERMEDI	ATE MELTIN	G EVENTS	Tfinal melting	Th	ThCO2
		1								
HB1	6	S		-42	-33	-19		-1.8		
	8	S		-30				-1.7		
	1	P	-59	-48	-20	-8.5		0.9		27
	A	P	-69	-41	-33	-15		0.1		
	В	P						-6.4		
	C	Р								
	D	P				-		-12		
	Ē	P						-7.2		
	1	S	{		-16	-10.2		0.1	193	
	2	S	-57					0.7		
	3	S	-57						171	
	A	S						0.7	209	
	B	S						0.4		
	C	S						0.5	203	
HB1 (II)	X				-11	-1.2		0.6		
	A				-19	-8.1	-1.1	1.6	221	
	3				-12	-4.8	-1.8		197	
	C							-1.1		
	D							-15.6		
	X	PS	-70	-53,9	-49	-37	-21.7			
HB1 (3)	1			-47	-34.6	-19.8		0.6	-	
	2		-61					-12,5		
	3		-62					-4.6		
	1		-40					0		
	2		-38					0		
	3		-30.6					0.1		
	i A		-79	-51				-39		
	В		-83	-51	-45			-39		
	1							-7.9		
	2							-7.9		
	1									

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Chapter 5 - Microthermometry Houtenbek

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	IN ERMEDI	ATE MELTING	G EVENTS	Tfinal melting	Th	•
HB1	1	P	-110		-29.6	+23		-15		
	2	P	-65		-39	-26.4	-10.5	-4	175	
	3	P	-65	-48	-33	-26.1		-28,8		
· · · · · · · · · · · · · · · · · · ·	4	P	-65	-48)	-24				
	1	S	-90	-45	-26		·	-15		
	2	S		-45	-36	-26	-21	-19.4		
······································	3	S		-45				· .		
	4	S	 	-45	-26	-21				
······································	5(x3)		-93	-45	-21	-8		-4.2	175	
HB1 (I)	1	P		-31	-7.3	-2.3	7	0.1	141.6	
	2	P				-2.3		0.1	161	
	3	P		-31				0.1	244	
	4	P							180	
	1	P	-56	-43				-18	j	
	2	14	-54	-30	-23	-14,4		-4.2	}	
	3	P						-24	}	
·· <i>··</i>	X	S	-54	-31	-24	-14	-6.2	-4	}	
······································	Y	S	-54	-31		·		-4		
HB1(I)	M		-70	-37				-4.4		
	N		-54	-34				-11		
HB1 (II)	A	P	-58	-51	-35	-26	-8.4	-6	241	
	B	P	-88	-51	· · · · · · · · · · · · · · · · · · ·	-22		-15	241.3]	
	D	P	-75	-50	-37	-18	-13	-7.2		
	E	P		-54	-32	-28	-24	-18		
	F	P,				-8		-2.8		
HB1	A1	S	-75						70,4	
	A2	S	-75	>-38	-20					
	A3	S	-75	>-38	-20			-4.4	173	
	B(X3)	S	-75	-41	-20	}		-8.6	202	
	A	S		-23	-9			-0.5		
	B	S		-23	-9			-0.6	1	
	C	S						D.1		
	D	S						0.1		
	2	S								
	5	S		-48	-21	-6	[· ·		

Chapter 5 - Microthermometry Houtenbek

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	Intermediate 1	nelting event	s	Tfinal melting	Th
	5	S	-52	-42	-28	-21		-15	137
	6	S	-52	-42	-28	-21		-8.3	181
RP11 11A	A	?						-22.3	168
	B	?						12	143
RP11 11A	1	?		>.46	-37	-24		12.5	96.4
	2	?		-44				9,2	
	3	?		-44			····	-9	į
·	4	?							131
· · · · · · · · · · · · · · · · · · ·	5	?						-0.5	135
RP11,11A	1	S		·		······································			143
······································	2	S	- <u></u>			[]		-11.4	114.3171
RP1: 11A	A	P		-50	-31				114
······································	В	P		-50	-31			-11.2	115
	C	P		-50	-31			-6.4	154
		S	-50	?		-25	-19.5	-6.3	
RP1 11	A	S	-42		-33	{		-7.5	200
Field 1	F	S	-42					-8.5	207
Vein 1	G	S	-64		-56	-35		- 18	
	1							3	
RP1 11	A (X500)	P	-44					-1	161
Field 2	B	P	-39					-7,3	
··	C	P	-47					5.3	165
RP1 11		P	-40					-0,4	122
field 3 a		P	-40					-3.1	109
		P		-40				-3,1	109
field 3b		P		-42	-30			-5.9	130
						1		-5	140

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	Intermediate r	nelting event	s	Tfinal melting	Th
RP11 11A	1	?	-51	-42	-30	-23	-18	-12	
	2	?	[-51;-58]	-42	-30	-23	-18	-11.8	
	3	?	[-51,-58]	-42	-30	-23	-18	-17	121
	4	?	[-51;-58]	-42	-30	-23	-18	-15	127
	5	- 7	[-51;-58]	-42	-30	-23	-18	-8.2	128
	6	?	[-51;-58]	-42	-30	-23	-18	-5.5	<128
	1 1	?						-0.3	
	2	?						-3	
	3	?						-2	99
	4	?						-6.5	139
RP11 11A	[1]	P	-54.5	-50	-44	-33	-22	-8.9	214
FIELD 1	2	P	-53	-50				-17.3	169
	3	P	-53	-50	· · · · · · · · · · · · · · · · · · ·	·		-13.9	154
- <u>_</u>	4	P		-50	· · · · · · · · · · · · · · · · · · ·			-1.8	
	B	S	-65	-50	-36	-29		6.6	126
	<u> </u>	<u> </u>	-68	-46				11.7	128
	C	<u> </u>	-69	-46	<u></u>			10.4	128
	3	S	[-51;-64]		·			13	147
·	<u>4 (X100)</u>	S	[-51;-64]	-40				-3,6	
		S		-54,5	-21	·		-18	138
·······		S		· <u> </u>				-16	182
	A	S		-54	-28			13.4	
	<u> </u>	S			<u> </u>			16	
RP11 11A	1	5	-69	>-36	-36	25		-22,3	159
	<u>^</u>	P	-53					-21	
	B	P	-44	-52	-36	-27	-20	-7.4	
	<u> </u>	<u></u> P	-82		<u></u>			7.9	
	¥	م	-50	-37		· · · · · · · · · · · · · · · · · · ·	<u></u> ,	-9,5)	
	<u>Ę</u>	P	-53		· · · · · ·	ļ		-8	
· · · · · · · · · · · · · · · · · · ·	G	<u> 4</u>	-63		·			-11	
			-50					-6.9	
RP11 11A		S		-42	-28				121
		<u>S</u>	-52	-42	-28	-21		-12	
		<u>s</u>	-52	-42	-28	-21	<u> </u>	-18	125
	4	S S	-52	-42	-28	-21	ł	-21)	137)

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	Intermediate r	nelting even		Tfinal melting	Th
A\$26 10C	1		-43	-40	25			5.1	
	2	_		[-3,9	
	3	·						0.3	
	4							-0,8	
· · · · ·	5							-2.4	
	1		-43				··· = ================================	1,6	
AS26 10C	2		-43	<u> </u>			······································	1	
FLUORITE	X10		-43		······································			[-1.5;0]	
······································		S	-47	-38	-20	-12	·	1	
	11	S		<u></u>				-1	
CHIP1		S	[-46:-56]	1	······			-8,8	
······································		S	I-46:-56]				, <u></u> _	-4.2	
		S	[-46:-56]	·····		····		-4	
·		S	[-46:-56]	· · ·		·····		-2.8	
		S	[-46;-56]					-2.8	
······································	1	S	[~46;-56]		*****			-1.3	· ,
······································	· · · · · · · · · · · · · · · · · · ·	S	[-46;-56]	1		· ·		-0,2	
	····	S	[-46;-56]	1	······			0.2	
*************		S	[-46;-58]						· · · · · · · · · · · · · · · · · · ·
AS26 10C	A	?P	-37	-34	-23	-18	-12	-3.5	243
CHIP 2	D	·	-37	-34				-1.4	140
fluorite ass	E							-3.5	
with chi &aspy	F				· ·	ļ — — — — — — — — — — — — — — — — — — —		-2.2	145
	В					[122
<u></u>	X30	S	-45	-31	-22	-5,1	-2,1	-1.7	235.8
RP11 11A	A	P			-28	-24		13.Đ	95
vein qz ass	D	P							
withpy	F	S	-74	-45	-32	[-8.1	168
	G	S						-4.3	168
								-10.3	
								-8.4	
RP11 11A		S	-76	-45	-30	-24	-23.5	-7.6	99
		S	-51	-41	-34	-24		-8.2	

Chapter 5 - Microthermometry Albert

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	Intermediate n	nelting event	5	Tfinal melting	Th
RP2 20B	X17	S	-40	-33	-27	-21.7		-3,1	
FLUORITE		S	-40					-5,3	
		S	-40					-4.1	
	E	S	-38	-33	-30	-25.6	-20	-3.2	
	B	S	-38		-26			-13	
	A	S	-62	, <u> </u>				-5.2	
	C,	S			-26				
	D)	S						[
······································	B	S	-39		-30			0	
	A	s	-48			······		-8,1	
RP2 20B	A	S	-50	-38	-27,1			-4.8	273
	B (X100)	S	-50	-38	-28			[-2.6;-1.7]	[71;93]
	X	Ś	-49	-34	-20,9	-15		-4.8	111.9
	j Dļ	P	-78	-41	-29			-8.8	116
	B	P	-78					-6,8	
	C	P	-78						
	A	P	-78					-20.5	199
		P	-83					-4.3	
RP2 20B	1		[-42;-47]	-49	-32	-24		-13,5	171
field 3	5		[-42;-47]			•		-5,8	
fluorite	6		[-42;-47]					-15	
···	7		[-42;-47]			1		-12.4	
· · · · · · · · · · · · · · · · · · ·	8		[-42;-47]	}	·		·	-10	
······································	10		[-42;-47]	-50	-37	-26	}	-6.1	69.3
	11	······································	[-42;-47]					-14	>262
	12	····	[-42;-47]					-10)	>263
	13	·	[-42:-47]	-49	-42	-30	-24	-10.1	200
RP2 20B	1(x100)	S	-54	-52			1	-13.4	[70;240]
field 4	2		-54	-52			1	-11	[70;249]
	3		-54	-52				-11	234
	4		-54	-52	· ·			-9.8	[70;240]
				}					
				}					
				1		}			

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	Intermedia	ite melting	events	Tfinal melting	Th
RP2 27/9	A	S	-63	-46				-13.5	147
CHIP1	B	S	-62				·	-15	98,9
	A	S	-63	-59	-40	-31		-18.1	137
	E	Ş	-70	-59	-40	-31		-24.5	150
RP2 27/9	{L	S	-62	-36	-31	-24		-12.2	
	К	S	-62	-36				-12.3	
	Ň	S	-63	-36				-11	
	C	S	-63	-41					108.
		S	-49	{				1.9	
	X	S	-77	-59	-40	-31		-26	
	1	S	-77	>-41	-30	-23.8	-16		
	2	S	-77	>-42					
	Y	S	-77	>-43					
	A	8		>-40	-30				
	B	S		>-40				-10	155
		S		>-41				-10	159
		S		>-43				-3.6	
	F	S	-32	-55				14	143
	D	S		-55				-10	175
	E	S		-55				-10.2	
								9.2	225
					}			3	135
RP2 27/9	B		-49					-6,9	191.8
	1							-4.9	
	C								195
	D		-69					-7	195
	1							-6,5	181
	A		-49	-48,4	-46	-45	-27	-6,5	
	1		-51					-11	225
	1		-50.9	-57	-49	-41	-26	-7.3	
			-74		{			-18	191
	}			-57				-5.3	<191
RP2 27/9		S		<-44	-29				135
		S			1			-7.8	
		8						-6.9	-

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	intermedia	te meitinn	events	Tfinal melting	Th
RP1 11A	A	?P		>-47	-32			-5	147
Vein 2	В	?P	-42	>-48	-31	`		0	114
	Ċ	?P	-40	>-49	-30		· · · · · · · · · · · · · · · · · · ·	-5	
	D	?P	-50	>-50	-29				156
	}E	?P	-50	>-51	-28	·		-2	
RP1 11A	1 (X3)	······································		· · · · · · · · · · · · · · · · · · ·				-5,1	158
	2					· · · · · · · · ·		-5,3	156
	3			}				-2.1	104
· · · · · · · · · · · · · · · · · · ·	4								
RP1 11A			-39	-38	-33	-16		-4.8	131
	D			L				-5.4	171
	B			1				-1.2	104
<u>RP1 11A</u>			-37		-36	-25		-6.4	-
Vein 3			-37	<u> </u>	ļ			-7.8	134
	<u></u>		-40.7		 		·	-7.8	120
	<u> </u>	·····			<u> </u>			-6,2]	152,9
	·	·····	-43	·	-37	-31	·····		119
	·	 	-38		<u> </u>		L	-24]	103
RP2 27A	<u> </u>		-48.1	-46	-44	-20.7	-16,6	-4.2	
CHIP 1	1	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	-60	-52	-33	-28	-24	+	131
	2	P		-52				11.9	134
	3	<u> </u>		<u> </u>	{ }			12.5	133
	4	<u> </u>	-66					15.3	14/
	5	بر			+				10
BD0 071			-/0	12-50	-43	-33	-2,3	0.0	119.7
	·	<u> </u>	-00	-10	<u> </u>			4.3	179
	┫━━━━━┤━		-14	<u></u>	<u>+</u>	└ ────	<u>,</u>		120
·	╸ <mark>╴╶╴╍╴┈╶╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴╴</mark>	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	-38	·	{			-2 5	158
· · · · · · · · · · · · · · · · · · ·	╊ ┈╸╸╸╸╸╸	2		┟────	<u>}</u> ≻-		<u></u>		
	-		·····	┤╌╘╌╶┉╌╌╼╌╸╴	<u>+</u>	[•••	<u>4</u>	128
·· <u>···································</u>	+	<u></u> 7	······	†	<u> </u>	<u>}</u>	<u> ^ ^ ^ ^ ^ </u>	╡╾┉╾┉╶┅╾┈╍╸┉┲╶┉┤╴	173
RP2 27A	·╋┯╾╷╾╵╼╌╼┶╤┈┶╌╶╼╌╼╌┶┝╵╌╸∲╌ ┃	Ś	-42	7-45		<u> </u>		7.2	113
CHIDA	+	2	-40		†	-23		-0.4	1116

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	INT RM	EDIATE	MELTIN	Tfinal melting	Th
T801	A	S	-59	-37.5	-27	-23		-11.9	148
QUARTZ	B	S		-49.5				-22.2	>110
CHIP 1	C	3		-49.5				-17.6	
	D	S						-17	
	A	S	-65	-29	[-20,9	102
	B	S	-74	-29			······		110
	A	S	-56	-33				-11.4	70
	B	S	-58	-33				-11.2	72
	4	S		-23	-19			6,4	138
	A	P	-62	-44.8	-25	-21		16	200
CHIP 2	1,2,3,4	5	-62	-58	-32	[-16	
QUARTZ	A	S	-55.8	7-28				-13.4	122
	A	S	-61	-30	-21			-12.9	187
	B	S	-59		1			-12.9	85
	C	S	-57.7	-30	-21			-12.9	
······································	1,2		[-33	-21			-10	149
	3	S	-66	{	-21			-14	100
CHIP 3	1		<u> </u>						
TOURMALINE	A	S	-52	-44.6	-41	-31	-10	-9.7	82
······································	B	P	·	}				-12.7	85
QUARTZ	A	P	-62	-35				-14.3	115
	B	P	<u> </u>	{				-12,7	115
CHIP 4	A	S		-47				-10	122
	C	S		-36	-24	-22		-20	86.5
********************************	D	P	1	-36	-24	-22		-15,1	156
······································	E	P	1	-36	-24	-22		16.5	140
	F	P		-36	-24	-22		15.3	187
					· · · · · · · · · · · · · · · · · · ·			*	
WG35		· · · · · · · · · · · · · · · · · · ·		[]	1			
FIELD 1	ZONE (X9)	P	?	?-50	-30	-24		?	
FIELD 2	ZONE (X9)	S		?	?	?	?	?	?
FIELD 3	TRAIL (X10)	Ş	-42	-35	-30	-24	-19	-5.1	
	TRAIL A	S	-73	-51	-44	-23		2.9	123
	В	S						6.1	128
	TRAIL (X7)	S	-75	-47	-21.1				71

SAMPLE NO.	INCLUSION	ORIGIN	Tfreeze	Te	INTERM	DIATE	MELTIN	Tfinal melting	Th
WGA35	A	?	-80	-55	-44			-23	160
FIELD 1	B	?	-60					-23	160
	C	?	-60					-23	160
	D	?	-60					-20	78
	E	?	-60					-19	94
	F	?					·	-21	
	G	?						-18	
	Н				}			5.9	135
FIELD 2	A	S	-65	-55	-43	-34	-23	-25	146
	В	S	-65					-14.2	162
	C	S	-65					-14.6	161
	Ď	S	-65						149
	E	S	-65					-24.7	125
	X	S	-65					-14	
	В	S	[-16	143
	Ċ	S	1		[70
	D	S			[·····]			-10,1	146
	A	S	-75	-54	-31	-24		-17.3	
	В	S	-73	-54	-31	-24	:	-19,4	148
	C	S	-75	-54	-31	-24		-21	164
<u> </u>		*********	1						
WG03	1	S	-52	-50	-43	-36	-9,6	-6.2	
FIELD 1	2	S						-6.2	
·	3	S	-46					-2	
FIELD 2	F		·	-51	1			>0	
	1	· • · · · · · · · · · · · · · · · · · ·		-49.5	-45	-38.5		>0<	· · · · · ·
	н							0.4	

RESULTS OF THERMAL DECREPITATION ANALYSES OF SAMPLES FROM GRASS VALLEY.

SAMPLE	T(°C) OF	MASS DETECTED	COMMENTS	
	DECREPITATION			
GV01	100-150	44 (CO ₂ ⁺ /N ₂ 0 ⁺)	Gradual increase of	
		28 (N2/C2H4*/CO*)	background.	
		18 (H₂O⁺)		
	170	2 (H ₂)	Single inclusion burst.	
	181	40 (Ar*)	Ar reaches peak at 200°C,	
			then starts declining	
			rapidly.	
GV02	85	44 (CO ₂ ⁺ /N ₂ 0 ⁺)	Gradual increase.	
	118	12 (C ⁺)	Single inclusion burst	
		16 (O ⁺ /CH₄ ⁺ /NH₂ ⁺)	containing methane,	
	· .	15 (CH₃⁺/NH')	•	
	206	44 (CO ₂ ⁺ /N ₂ 0 ⁺)	Whole series of small	
		28 (N ₂ /C ₂ H ₄ ⁺ /CO ⁺)	barsts.	
	· ·	16 (O ⁺ /CH ₄ ⁺ /NH ₂ ⁺)		
		12 (C ⁺)		
		18 (H ₂ O ⁺)		
		34 (H ₂ ³² S ⁺ / ³⁴ S ⁺)	Note presence of S.	
		48 (SO ⁺)		
	363	15 (CH ₁ ⁺ /NH ⁺)	Series of small bursts.	
		16 (O ⁺ /CH, ⁺ /NH ₂ ⁺)		
	· ·	28 (N2/C2H4+/CO+)		

RESULTS OF THERMAL DECREPITATION ANALYSES OF SAMPLES FROM GRASS VALLEY (CONTINUED).

SAMPLE	T(°C)	MASS DETECTED	COMMENTS
GV05i	138	12 (C*)	Single inclusion burst
		15 (CH ₃ */NH*)	
		16 (0 ⁺ /CH ₂ ⁺ /NH ₂ ⁺)	
		44 (CO ₂ ⁺ /N ₂ 0 ⁺)	
	169-300	44 (CO2 ⁺ /N20 ⁺)	Small peaks which increase in intensity
•		15 (CH3 ⁺ /NH ⁺)	between 182-300°C.
			Large inclusions burst followed by a
	322	12 (C*)	series of smaller bursts which cease by
· · · ·		16 (O ⁺ /CH ₄ ⁺ /NH ₂ ⁺)	473 °C.
		28 (N ₂ /C ₂ H ₄ ⁺ /CO ⁺)	
· · ·		44 (CO2 ⁺ /N20 ⁺)	
GV052	115	16 (O ⁺ /CH ₂ ⁺ /NH ₂ ⁺)	Increase in back for water peaks.
(quartz 1,2 & 3)		18 (H ₂ O ⁺)	CO ² and Ar curves gradually increase
	160	44 (CO ₂ ⁺ /N ₂ 0 ⁺)	No discrete fluid inclusion bursts in this
	· .	40 (Ar [*])	sample. All curves return to background
			at 400 °C.
GV053	7 9	44, 15	Small methane and nitrogen peaks
(Quartz 7)	·		N2 increasing.
	125	14, 28,44, 15	2 small peaks followed by a series of
· · ·	148	44	others.
			Large CO_2 peaks. N_2 has returned to
	194	44	background.
			Ar increasing rapidly. CO2 diminishing
	250	40, 14, 15, 32	First water peak.
			Water peaks and second batch of CO
	285	16, 18	peaks.
GV053	300	16, 18, 44	Water decreasing, and small CO_2 peaks
continued			continuing.
	400	16, 18, 44	CO2 peaks continue until 500 °C.
	500	44	

RESULTS OF THERMAL DECREPITATION ANALYSES OF SAMPLES FROM GRASS VALLEY (CONTINUED).

SAMPLE	T(°C)	MASS DETECTED	COMMENTS
GV054	100	18,16	Gradual increase of H ₂ O.
•	201-220	12,14, 28, 30	Background of 12,14, 28 and 30 starts
			increasing.
	293	18, 16, 44 28	Large water burst with 44 and 28.
	• • •		Response starts decaying by 322 °C and
			is back to background by 400 °C.
GV056	97-125	28	Gradual increase in 28, which reaches
(quartz 6, 7 & 8)			peak at 114, and then decreases to
			background.
	130	44 16, 18	First CO2 peak. Water rising.
	240	44, 16, 18	CO2 and water bursts. CO2 peaks larger
			than water peaks.
	312	40	Ar background increasing.
	312-533	44, 16, 18,40	CO ₂ and water bursts continue until
			533°C.
GV057	96-500	44, 28, 14	N2 and CO2 peaks. No water response,
(quartz 8)			. • .

RESULTS OF THERMAL DECREPITATION ANALYSES OF SAMPLES FROM ALBERT.

SAMPLE	T(°C)	MASS DETECTED	COMMENTS	
RPI 11a	138	18	Water starts increasing, and continues until	
quartz yran			400°C.	
with sulphides	400	33, 36	H2S and HCl start increasing.	
RP1 11	11 7	18, 16	Water curves start increasing.	
Quartz vein 1	254	14, 28	Nitrogen curves increasing.	
	303	14, 15, 28 , 44	Small inclusion bursts.	
	350	36, 33	H ₂ S and HCl start increasing gradually.	
			Water curves start decreasing.	
· ·	420	16, 18	Small argon spikes.	
	454	40		
RPI 11	86	14, 28, 44	Broad nitrogen and carbon dioxide curves	
Quartz vein 2			(first CO₂ pulse).	
	110	18	Water increasing.	
•	256	18	Water reaches plateau.	
	314	18	Small water peaks on back of plateau.	
	350	33, 36	HCl and H ₂ S start increasing.	
	381	44	CO_2 background increased (second CO_2	
	450	44, 18, 16	pulse)	
			Small CO2 peaks (third CO2 pulse), and	
			rapid increase in water response.	
RP1 11	80	28, 44, 14	Nitrogen and CO2 curves start increasing.	
Quartz vein 3			Nitrogen and CO ₂ curves start decreasing.	
	100	28, 44, 14	Water starts increasing.	
			Nitrogen curves increase again,	
•	110	18	Increases.	
	242	28, 14	All curves return to background.	
	295	44		
	400		· · · · · · · · · · · · · · · · · · ·	

RESULTS OF THERMAL DECREPITATION ANALYSES OF SAMPLES FROM SPOEDWEL.

SAMPLE	Τ(°Ϛ)	MASS DETECTED	COMMENTS
L1	83	14, 28, 44, 15	N2 and CO2 curves start increasing.
			Water and argon peaks start increasing and
	100	18, 40 .	nitrogen and CO ₂ peaks start decreasing.
			Broad CO ₂ peak.
	· ·		Start increasing again.
	138-150	44	Small water peaks.
	245	14, 15, 40	H2S and HCI start increasing,
	268	18	
	300	33, 36	

ABSTRACT

The Nature of Hydrothermal Fluids Associate ' with the Granite-hosted Spoedwel Copper Mine, Bushveld Complex, South Africa.

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The Spoedwel Copper Mine is situated on the farm Spoedwel 701ks, in the Groblersdal District north-west of Marble Hall. The copper mineralization occurs in the upper portion of the Lebowa Granite Suite (Nebo, Klipkloof and Makhutso granites), and is hosted by de-silicified mediumgrained brick red granite, often referred to as an "episyenite" (Scoggins, 1991).

The aim of this research is to elucidate the nature of the various fluids that traversed the granite pluton in the Spoedwel region, by determining the physical and chemical properties of the representative fluids trapped in fluid inclusions. The relationships between the individual fluid inclusion populations and the different pulses of ore deposition and alteration consitutes an interesting avenue of research.

The ore suite at Spoedwel is dominated by copper-bearing minerals, the most abundant being chalcopyrite, which is altered to bornite, chalcocite and covellite. The occurrence of tetrahedrite is erratic and present in minor amounts. Pyrite, sphalerite, and galena are less abundant than chalcopyrite, but never the less, form an integral part of the paragenesis at Spoedwel. Cassiterite, zircon, magnetite and sphene occur as accessory minerals, which crystalized syngenetically within the Spoedwel Granite Pluton. The Cu-Fe-Zn-S mineralization occurred later and is related to de-silicification, chloritization and haematization of the granitic host rock. The introduction of secondary fluorite occurred after extensive haematisation of feldspar crystals. Haematite veinlets are transected by younger quartz and fluorite veinlets, in which several fluid inclusions contain trapped daughter crystals of haematite.

The overall paragenetic sequence is as follows:

pyrite (white-ish yellow), cassiterite, zircon and sphene forming the orthomagmatic suite, followed by pyrite (yellow), sphalerite (transparent), galena, tetrahedrite, sphalerite (opaque) and chalcopyrite. This secondary ore suite is associated with several episodes of alteration which resulted in the conversion of chalcopyrite to bornite, chalcocite and covellite.

However, as the above sequence of mineralization suggests, ore deposition at Spoedwel is rather complicated, with more than one phase of over-printing evident. Two generations of pyrite and sphalerite are discernable, as well as two generations each of the gangue assemblage quartz, feldspar, chlorite and fluorite.

A thorough examination of polished thin sections and doubly polished thin sections (wafers) has confirmed that several different generations of fluid were responible of the formation of the deposit as it occurs today. Fluid inclusions have been observed in quartz, fluorite and transparent sphalerite crystals, preserving fractions of the magmatic fluid as well as some of the other later metamorphic fluids. Fluid inclusions in cassiterite are scarce and too small to provide meaningful analytical results.

Fluid inclusions have been categorised as primary, secondary or pseudosecondary according to the scheme of Roedder (1979) and inclusions large enough to observe phase changes in the components, and hence be suitable of microthermometric analysis, have been located and mapped. The presence of variable phase proportions in the inclusions suggests that boiling or effervescence of certain of the fluids was in process at the time of entrappment. Inclusions containing a single phase (either liquid or vapor) are found in close association with two (L+V) and three (L-V+S) phase inclusions (Plate 1). Primary inclusions, occuring random 'y scattered within grains, or lining and radiating from growth zones, commonly contain cubic haiite and/or rounded sylvite daughter crystals (Plate 2). However, at least four other crystals, whether as true daughters or as trapped crystals have been noted in single inclusions. Positive identification of halite, sylvite and haematite crystals have been made, and the presence of sulphides, muscovite and chlorite is suspected. Later generations of fluid are less saline, and contain no daughter crystals (Plate 3).

The composition of the fluid phases within fluid inclusions were investigated by means of Laser Raman Spectroscopy. Spectra obtained from selected primary, secondary and pseudosecondary inclusions indicates that nitrogen was an important component of the system. The presence of carbon dioxide, water, and methane was also detected.

The results of this study are potentially valuable as aids in exploration for ore deposits in the nearby vicinity, as well as contributing to the existing database (eg. Ollila 1981; Pollard *et al*, 1991) from which a model of the mineralization in the Bushveld granites may eventually be constructed.

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List of Plates

- Plate 1: Photograph showing variable phase proportions in primary fluid inclusions lining a growth zone in a euhedral quartz crystal.
- Plate 2: Photograph showing a portion of a pseudosecondary trail of inclusions in quartz containing large anisotropic sylvite daughter crystals.
- Plate 3: Photograph showing a trail of secondary inclusions in fluorite containing no daughter crystals and variable phase proportions.



Plate 1:

Plate 2:

Plate 3:

FLUID MIXING AND THE FORMATION OF POLYMETALLIC MINERALISATION IN THE BUSHVELD GRANITES.

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Numerous small base metal deposits are known to occur in the acidic rocks of the Bushveid Complex and modern exploration programs are currently re-examining this metallotect in an attempt to refine the current working hypothesis for mineralisation in these granites. The hypothesis proposed for the origin of mineralisation is multifaceted, encompassing both spatial and temporal relationships between at least three episodes of ore formation. The first episode of mineralisation (typified by the Zaaiplaats Sn deposit) occurred at relatively high temperatures (ca. 600°C to 400°C), and resulted in the formation of orthomagmatic cassiterite, scheelite and an early generation of fluorite. At lower temperatures (200°C<T<400°C), where processes where essentially fluid dominated, a mesothermal Cu-Pb-Zn-As-Ag-Au assemblage was deposited (exemplified by the Spoedwel, Boschoek and Albert Cu and Ag deposits). A third episode of mineralisation resulted in the formation of an Fe-U-F assemblage and is recognised at several, but not necessarily all, of the deposits examined (for example, the Albert Ag deposit). The extended nature of this three-stage paragenetic sequence is considered to reflect widespread mixing between an early fluid derived by H2Osaturation of the granitic magma and a meteoric fluid, circulation of which was stimulated by the long-lived high heat-productive capacity of the Bushveld granites, as well as exhumation of the metallotect. Support for this hypothesis is discussed below-

1) Cathodo-luminescence images have indicated the presence of two major episodes of fluorite precipitation at Spoedwel. An early, possibly magmatic, stage formed as a result of cooling of acidified brines, whereas a later, low temperature, stage is believed to have precipitated as a result of progressive mixing of this brine with a connate component.

2) Coveliite over-printing of Cu-bearing sulphide minerals along grain boundaries and microfractures is characteristic of retrograde thermal processes. Dissolution and replacement of chalcopyrite by covellite is considered to be the result of the imposition of an oxidizing fluid, and not simply lower temperatures.

3) Local occurrences of hydrothermal tournaline veins and spheroids, similar to those of the Sn-W-Cu deposits of Cornwall (southeast England), have been recognised in the Bushveld granites. In both cases the interaction of boron-rich, magmatically derived fluids, and Fe-Mg-rich connate fluids is thought to have resulted in localised precipitation of tournaline.

4) Both hypersolvus (single feldspar) and subsolvus (two feldspar) granites are now recognised in the Bushveid Complex. Subsolvus mineralogy has been identified at the Spoedwel, Albert and Grass Valley deposits, while the hypersolvus granities tend to be unmineralised. Coexisting hypersolvus and subsolvus granites are interpreted as being the products of meteoric water incursions.

5) Fluid inclusion characteristics suggestive of fluid mixing include; a) the occurrence of monophase liquid- and vapour-rich inclusions within two and three phase fluid inclusion assemblages which have variable phase proportions; b) broad ranges

of salinities, densities, and homogenisation temperatures in single fluid inclusion assemblages; and iii) the presence of **nitrogen**, **methane**, other **heavier hydrocarbons**, as well as elevated Ar contents in the fluids (Table 1 and Fig. 1) which have been detected by Raman Spectroscopy and Quadrupole Mass Spectrometry (QMS).

6) Fluid mixing is also indicated by the stable isotopic signatures of fluid inclusions. δ^{13} C values indicate at least two sources of carbon, viz. from limestones and from an externally derived organic carbon. In addition, δ^{16} O and δ D values fall in a range outside that characteristic of purely magmatic fluids.

Table 1. Selected QMS analyses of fluid inclusion decrepitates from various deposits, compared to a barren granite sample. Analyses in mole %.

	CH	C.H.	Ar	N,
GRASS VALLEY (GV02)	2.9x103	_3.7x10*	2,1x10°	5.1x10 ²
TOURMALINE SPHEROIDS	5.1x10 ²	_2.8x10*	4.8x10 ^a	7.2×10*
ALBERT SILVER MINE (RP2)	1.3x10 ²	6,5x10*	4.1x10°	7,3x10 ²
SPOEDWEL MINE (SP5)	2.8x10 ⁴	4.2x10*	1,9x10 ³	1.7x101
KLIPKLOOF GRANITE	0.0	3.240*	4.4x102	9.4x10*



Figure 1. Raman spectrum of a fluid inclusion

The early high temperature (ca. 600°C) Sn-W assemblage was precipitated by orthomagmatic processes, as well as the circulation of magmatic fluids. With time, the pluton cooled and was subject to regional uplift and erosion. Fractures developed, acting as conduits for external fluids of meteoric and/or connate origin. The late magmatic fluids, enriched in incompatible metals (and volatiles), interacted with the connate/meteoric fluid, of contrasting chemistry and possibly also metal-charged, resulting in the localised precipitation of a secondary, lower temperature (>200°C) mineral assemblage (Cu-Pb-Zn-As-Ag-Au) in the zone of fluid mixing. As the external fluid component became progessively more dominant, the late Fe-U-F (>140°C) paragenesis formed. The extended paragenetic sequence in the acid rocks of the Bushveld Complex is adequately explained by a combination of orthomagmatic processes and sub-solidus fluid mixing.

METALLOGENY OF THE ACID PHASE OF THE BUSHVELD COMPLEX

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The acid phase of the Bushveld Complex comprises a large sheet-like batholith of fractionated, alkali felspar rich granite-the Lebowa Granite Suite- intruded into a 4600m thick extrusive sequence of mainly rhyolites and pyroclastics - the Rooiberg Group. The latter was emplaced at 2061±2 Ma, while the final pulse of granite emplacement had occurred by 2054±2 Ma, Rb-Sr and Pb-Pb isotopic systems remained open for several hundred million years after emplacement indicating slow cooling and extensive fluid circulation related to the large radiogenic heat productive caracity of the mineralized portions of the batholith (up to 30μ W.m⁻³)

The acid rocks are characterized by innumerable small-to mediumsized polymetallic deposits which reflect the alkalic magma composition, the high degree of in situ crystal fractionation and the extensive circulation of hydrothermal fluids that has occurred. A complex paragenetic sequence, comprising (Sn-W)-(Mo-Cu-Pb-Zn-As-Au-Ay)-(Fe-F-U), reflects multi-facetted control of ore deposition related to incompatible element concentration daying crystallization, fluid circulation and concentration in the apical portions of the intrusion and focusing of fluid egress by major structures active during and after Bushveld emplacement. The extended paragenetic sequence, which ranges from orthomagmatic processes (Sn-W) to epithermal conditions (Fe-F-U), appears to have lasted for up to 1000 million years and is best explained in terms of long-lived, radiogenically stimulated, fluid circulation in which a dominantly magmatic fluid phase was progressively diluted by meteoric or connate components. Detailed fluid inclusion studies clearly demonstrate the characteristics of the fluid components involved in Bushveld metallogenesis.
Author: Freeman, Lauren Anne. Name of thesis: The nature of hydrothermal fluids associated with granite-hosted, polymetallic mineralisation in the eastern lobe of the Bushveld Complex.

PUBLISHER: University of the Witwatersrand, Johannesburg ©2015

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