GEOCHEMISTRY OF SINTERS OF THE ALKALINE CHLORIDE HOT SPRINGS IN THE ROTORUA GEOTHERMAL FIELD

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ABSTRACT

Sinters around the active geothermal springs at Rotorua consist of amorphous opal-A (except those around the Ngararatutara spring, which have in addition various amounts of chalcedony). Fossil sinters consist of opal-CT. Trace element analyses of the sinters show enrichment of As, Ga, Tl, Ge, Hg, Sb, W, Mo, Ag and occasionally Au. The fossil sinters have in comparison a much lower water content and are in comparison depleted of Al, Fe, Mg, Ca, Na, K and P and the traces of As, Ga, Tl, Ag, Sb, Mo and Pb, all due to leaching of sulphates or destruction of sulphides. Ge, Hg and W are not depleted. The presence of up to 17 ppm Ge in the SiO_4 lattice is indicative of rapid drop in temperature and pressure of the geothermal fluids.

1. INTRODUCTION

Quartz has only a small tolerance for trace elements and also a limited capacity for inclusions. As part of a general study of the chemical composition of primary and secondary quartz associated with mineralisation *silica sinters* of the Rotorua geothermal areah were analysed, where traces of gold and silver had been reported (Lindgren 1933).

The field work for this investigation contrasted silica sinters from active springs against fossil sinters. In addition coatings, sludges and coloured sinters were collected, which were analysed by optical emission spectroscopy. It was followed by microscopic examination, major and trace element analysis by XRF, scanning electron microscopy, mercury cold vapour analysis and XRD.

1.1 Geological setting

The Rotoroua caldera formed some one hundred and forty thousand years ago with the eruption of some two hundred cubic kilometres of ash of rhyolitic composition (Thompson 1974, Houghton and Brown 1985). The boundary of the resulting caldera, with a radius of 9.5 km, is largely defined by faulting. The present geothermal field covers approximately 10-15 km^2 in the southern part of the caldera.

1.2 Present geothermal surface activity

The surface activity of the geothermal system consists of hot springs, geysers, steam fumaroles and mud pools. Whakarewarewa, the last major geyser field in New Zealand, has some 500 pools, most of which are alkaline chloride, sometimes boiling, springs and at least 67 geyser vents, each with their own name. Because of thermal exploitation only seven geysers are currently active. The chloride water is neutral when deep in the system but becomes alkaline as it rises due to loss of carbon dioxide gas. The alkaline waters (pH 8-9) are saturated with silica, which results to the deposition of silica as the water discharges and cools. The also common acid-sulphate waters are primarily related by steam or low discharge such as fumaroles, steaming ground, turbid water and mud pools and will not be discussed here (Teece, 2000). A wealth of information on the chemistry of the Rotorua waters can be found in Glover and Heinz (1985). Listing of all the springs and their characteristics can be found in the Technical Report of the Geothermal Monitoring Programme 1982-1985 (Mahon 1985). See also Fellows and Bates (1998). New information on the general setting, bore field geology and volcanic history of the area has not changed in substance.

1.3 Locations

With a few exceptions all samples were taken from the Whakarewarewa geothermal area (cut by the Puerenga Stream). We follow in this study the established spring numbering system listed in Mahon (1985). The samples listed in this study are listed in table 1. For detailed sample site descriptions, maps and coordinates see O'Shea (1987).

1.4 Sinters

Samples were taken from newly-formed sinters of the alkaline hot springs Papakura, Pohutu, Rotarua Tamaheke and Ngararatuatara and of fossil sinters from the Te Aranata Cave, Wharerewa and the Utahina Valley. Papakura is in constant ebullition to 0.3m high and the spring has a temperature of 99°C. A large sinter mound with stalactites is associated. Up to 1979 Papakura was constantly spouting up to 4m. Pohutu on Geyser Flat is surrounded by a raised mound of salmon pink sinter. It erupts 25-45% of the day, usually to heights of 15-20m. The Waikite geyser last erupted in 1968.

Geyserite, geyser eggs and silica stalactites also form on Geyser Flat. Roto-a-Tamaheke is a 200m wide turbid lake with a temperature of approximately 50°C, although varying enormously from section to section. Ngararatuatara spring is approximately 2m x 0.5m with some ebullition. It is a clear spring with a temperature of 90°C. The spring has a raised rim around it composed of a delicate reddish brown sinter. There are two breaks in the rim that allow outflow of water from the spring and skins of purple material are found in these outlets as well as in the spring itself and on the rim. These skins are thickest in the outflows, and the material shows a distinct layering from a dark pink layer through orange to purple. The layers are all of a consistent thickness, ranging from 0.1-0.2 mm. A large associated sinter terrace is coloured orange due to the growth of algae on its surface kept alive by the outflow of water from the spring.

In areas of high flow rate dense vitreous sinter forms while more porous chalky sinters form in areas of low flow. (See Ihler 1979.)

Unusual sinters are located in the Ororea Group of springs. They occur mainly below the water level, contain a large percentage of organic material and are coloured black because of this. Small very finely layered stromatolitic

structures have been produced on the sinter surface. Thin sections show different colours, but electron microprobe proved that this is only due to the organic content of each layer. Similar sinters from the Utahina Valley and in the path cutting beside Roto-a-Tamaheke contain fine laminations and textures indicating cyanobacteria-induced formation also. Sinter is deposited from spring waters by both inorganic and inorganic processes.

Abiotic processes are dominant close to spring outlets where strong ebullition takes place, while biotic processes become more important at the outer edges and aprons of the springs. Silica sinter is white, colour variations caused by different amounts of impurities. Metastibnite is likely to be the cause of the salmon ink colour (T.M.Seward pers. comm.), included pyrite produces grey sinters and the black colour of sinter around the Ororea Group is caused by microbial growth. Sinters may also be coloured on the surface orange or green by cyanobacterial mats, such as on the sinter terrace associated with Ngararatuatara, which is orange.

2. MINERALOGY

2.1 Sinters

The X-ray diffraction patterns of the fresh sinters of Papakura, Pohutu, Roto-a-Tamaheke and Spring 493 are those of opal-A. However the newly-formed sinters of Ngararatuatara and Spring 374 consist of opal-A with some quartz and the most pronounced quartz peaks are present in the newly-formed material from the rim of the Ngararatuatara spring (sample 70222). The fossil sinters have the X-ray diffraction patterns of opal-CT: disordered *a*-cristoballite with *a*-tridymite stacking and some of the Wharerewa samples some opal-C but mainly well-ordered *a*-cristoballite. However, one of the fossil Wharerewa sinters consists of opal-A. These observations corroborate the *general* observation that in siliceous sinters that precipitate from hot near neutral alkali chloride waters the first formed silica phase in the residue consists of non-crystalline opal-A that subsequently crystallises to paracrystalline opal-CT and eventually to quartz (Cook et al. 2001, Lynne et al. 2005, Lynne 2007).

2.2 Other Surface Precipitates

2.2.1 Pyrite

A distinct mineral zoning was seen around a number of alkaline chloride springs, consisting of pyrite layers close to the surface outlet of the spring and sinter formation past this, with mixed layers of pyrite and silica in between, indicating separate deposition periods for the two phases. Above the level of the spring, pale yellow coatings have formed, presumably due to deposition from escaping hydrogen sulphide. Pyrite coatings feature at a number of springs, most notably at Springs 540 and 55, both of which are small, boiling springs on the banks of the Puerenga Stream. The pyrite forms in very thin layers, indicating that pyrite deposition may have been episodic. Pyrite grains, and pyrite coated grains and twigs were found in the sediment at the bottom of many of the springs including those located at the edge of the Puerenga Stream Springs 55, 540, 493, 300 and 296 and those at Ngapuna. The pyrite grains were approximately the same size as the sediment they were found in, ranging from very fine to a few millimeters. Most grains were euhedral in shape.

2.2.2 Sulphur

A layer of finely banded yellow sulphur, varying in thickness from 1.5 to 20 mm occurs above the water level at Spring 374, a large alkaline spring to the north of Roto-a-Tamaheke. It is amorphous to x-rays. The yellow sulphur coatings mentioned earlier, above the water levels of many springs are very conspicuous at Spring 540 and Spring 493.

2.2.3 Sulphates

Small flowerettes of fine crystals occur on the warm ground of the Puerenga Stream approximately two metres upstream from Spring 493. They occur in patches from white to yellow and brown, and in diameter from 0.5 –5cm. They are very soft and disappear after rainfall indicating that they are soluble in water. Rosettes of a similar nature were also noted beside the spring at the mouth of the Puerenga Stream at Ngapuna. Similar material was reported by Grange (1937). Samples of the white material (sample 70218) and the brown material (sample 70219) were analysed by XRF, infrared spectrometry and X-ray diffraction.The X-ray diffraction patterns of the two samples are rather complicated.The samples are a mixture of tamarguite $NaAl(SO_4).6H_2O$ and rostite $Al(SO_4)(OH).5H_2O$, with in sample 70219 further alunogen $Al_2(SO_4)_3.17H_2O$ and a less hydrated version of the mineral $Al_2(SO_4)_3.12H_2O$.

2.2.4 Cinnabar

Red mercury sulphide was recognized at Te Aranata Cave (sample 70230) and in sinter from Whareererewa (sample 70233), an outcrop of old sinters to the east of Geyser Flat. Sinter analysed from Ngararatuatara (sample 7022) had a high mercury content, which could be due to the presence of cinnabar.

2.2.5 Antimony and arsenic sulphides

A very thin, discontinuous layer of powdery red to orange-yellow sulphide occurs 4-6 mm beneath the surface of the sinter at the Ororea Group (sample 70213). A gas vent at Te Aranata Cave is surrounded by spongy white sinter with small orange and lead grey material thought to be orpiment and stibnite respectively.

2.2.6 Ferrihydrite

Analysis of the orange coating (sample 70241) on the bottom rocks in Lake Tarawera indicate a hydrated iron oxide or hydroxide. It may be ferrihydrite. See XRF analysis.

A selection of sinters were prepared as fused discs for major element analysis by XRF. Loss on ignition was determined by heating a known amount of sample overnight at 1000°C. The results are shown in the table 2 below. For trace element analysis of the same samples pressed powder pills were used. The results fore the limited number of elements analysed are shown in table 3. It appears that most trace elements are lower in the fossil sinters. In addition a set of different samples from sinters from active alkaline chloride springs were analysed for a wider range of elements by emission spectroscopy; the results for volatiles and complete burn, are shown in tables 4 to 7. Analytical techniques are given separately below.

3. CHEMICAL COMPOSITION

Table 1: sample and spring number, location

Sinters analysed by XRF (results in tables 2 and3)		
Sinters from active alkaline chloride springs		
70205	Papakura (Spring28)	sinter stalactite
70207	Pohutu (S 75)	sinter from mouth
70211	Roto-a-Tamaheke (S 337)	sinter from apron near Ororea group
70215	W of Roto-a-Tamaheke	sinter
70217	S 493 next to Puerenga Stream	sinter, next to stream
70221	Ngarartuatara (S 529)	sinter from rim
70222	Ngararatuatara (S 529)	sinter from outlet
70224	Ngararatuatara (S 529)	sinter from terrace, 8m from outlet
Fossil sinters		
70232	Te Aranata Cave	sinter
70234	Whareрewa	finely laminated sinter
70238	Utuhina Valley	sinter
Other samples		
70208	Waikite (S 126)	cinnabar bearing decomposed sinter from mound
70218	Spring S493 next to Puerenga Stream	white Al, Na sulphates, warm gound
70219	ditto	brown Al, Na sulphates, warm ground next to spring
70241	Lake Tarawera	orange coating on bottom rocks

Miscellaneous samples analysed by Emission Spectroscopy Volatiles & Complete Burn (results in tables 4 and 5)		
70210	Roto-a-Tamaheke (S 337)	black mud from in front of measure bar
70204	Papakura (S 28)	sinter from mouth
70223	Ngararatuatara (S 529)	loose rock, bottom of spring
70239	Ngapuna	black mud from large lake
70240	ditto	pyritised mud from same lake
70241	Lake Tarawera	orange coating on bottom rocks
70207	Pohutu (S 75)	sinter from mouth

Miscellaneous samples analysed by Emission Spectroscopy Volatiles & Complete Burn (results in tables 6 and 7)		
70227	Spring 540	sulphur coating
70229	Geyser Flat	white salt from caves beside Kereru
70214	Ororea Group	orange material through sediment beneath sinter
70216	Spring 374	yellow sulphur layer
70220	Ngararatutara	purple alumium coating from outlet
70218	Spring 493	white Al, Na sulphates, warm ground next to spring
70219	ditto	brown Al, Na sulphates, warm ground
70230	Te Aranata Cave	cinnabar and stibnite bearing sinter
70231	ditto	sinter
70228	Spring 540	pyrite coating from below water level
Spring 540 is next to the Puerenga Stream, halfway between Ngarartutata and Papakura.		
Spring 374 is near Roto-A-Tamahake		
Spring 493 is next to the Puerenga Stream 150m north of the Ororea Group.		

4. DISCUSSION

4.1 Chemical differences between sinters from active alkaline chloride springs and fossil sinters

The fossil sinters are in comparison very much depleted in the "major elements" Al, Fe, Mn, Mg, Ca, Na, K and P. These losses would be largely attributable to loss of sulphates. The considerable reduction in loss on ignition will be due to water and sulphate loss on ageing. The losses of the traces As, Tl, Ag, Sb, Mo and Pb can be all accounted for by leaching, as all their sulphides and sulphates, if existing, decompose or are (slightly) soluble in hot water and acids. A discussion of the mobility of these elements can be found in Nguen (2007) and Tanfu Xiao (2004). Ga will go together with the Al in the sulphates. Ge appears to stay in the lattice of SiO_4, and Hg and W are not depleted, respectively insoluble as cinnabar and tungstates.

Although Ge can be introduced to levels of thousands of ppm in artificially grown quartz, in natural quartz it is usually present at levels of < 2ppm. However, quartz in epithermal gold deposits contains several ppm Ge (Russell and van Moort 1999, van Moort et al. 1990).

GeO_2 is very much more soluble in water than SiO_2 at higher temperature. Consequently it is enriched in late magmatic and hydrothermal fluids. This leads to enrichment of Ge in quartz, sinters, sulphides and agate (Blankenburg and Schroen 1982). At relatively low pressure and temperature (700bars and 300^0C) germania solution in a-quartz occurs to about 24 mole%. Increasing the temperature to 750°C at the same pressure results already to increase in solubility of 31mole% (Miller et al. 1963). Although Li in the sinters could not be analysed, it is undoubtedly high as quartz in from epithermal deposits is high in Li (van Moort and Aung Pwa 1999). Li concentrations in water of the alkaline chloride springs at Rotorua (Glover and Heinz 1985) and other geothermal areas in New Zealand (Brown and Lloyd 1986) are very elevated.

4.2 Other precipitates

Trace element analyses of the sinters, precipitates and other surface deposits of active geothermal systems, show enrichment in As, Fe, Sb, Au, Hg, W, Tl and Ag. See summaries by Berger and Bethke (1983) and Brown and Lloyd (1986). The enrichments are not only due to direct inorganic precipitation of sulphides, tungstates, absorption by sulphides or hydrated iron oxides, but also of biogenic origin. The Ororea Group stromatolites at Roto-a-Tamaheke show silicified algal filaments as described by Jones at al. (2001) for Champagne Pool sinters at Waiatapu. Investigation by scanning electron microscopy of the layering of the stromatolites did not show inorganic differences, as one might have expected from the presence of orange material below the sinter.

4.3 Mineralogical differences between sinters

The predominance of Opal-A in the fresh sinters (like from the mouth of Papakura or the apron of Ororea) and of Opal-CT with disordered cristoballite in the fossil sinters at Te Aranata Cave or Opal-C with well ordered cristoballite at Wharerewa and the Utuhina Valley will be the consequence of recrystallisation as a function of ageing. However, the presence of fresh sinters consisting of opal with some chalcedony (Spring 374 and 529) to chalcedony only at the outlet of Ngararatuatara indicates that ageing is not the only factor determining type of silica polymorph. As direct formation of quartz does not occur under surface conditions the microcrystalline chalcedony at these springs appears to have been brought to the surface as a product of hydrothermal crystallisation of silica gel (Oehler 1976) at depth. This possibility was not further investigated.

4.4 Use in mineral exploration

The trace elements in paragraph 4.1 above other than W are used in mineral exploration as indicators of hot spring type deposits and the silicified zone, stockwork and quartz veins of deeper systems (Clarke 1989). To the list Ge should be added as it is so much dependent on the rapid decrease in temperature and pressure of the geothermal fluids. Similarly W should not be omitted. Both Ge and W are not affected by leaching. In a given situation the amount of Ge in the SiO_4 lattice (quartz or acid insoluble rock powders) correlates positively with the Au content of the ore (van Moort and Aung Pwa 2005).

5. CONCLUSIONS

Silica sinters proved to be a feasible low background sample medium. Even when fossil, the sinters from the alkaline chloride hot springs at Rotorua translate their epithermal origin through its high As, Ag, Tl, Sb, Tl, Hg Ag, Mo and occasionally Au content. The not-normally analysed elements W and Ge, together with Hg, are the most weathering resistant elements in the sinters.

The fresh sinters consist of Opal-A and the fossil sinters consist of Opal-CT. However, fresh sinters from the constantly ebullient Ngararatuatara spring contain appreciable amounts of amorphous chalcedony, presumably brought to the surface from below.

APPENDIX: ANALYTICAL TECHNIQUES

X-Ray Fluorescence

Samples for major elements were prepared as fused discs. The major elements Mg, Na, K, Fe, Mn, Ti, Si, Al and P were determined as oxides using a Rh tube. Samples for trace elements 5-6 g to make pressed powder pills. Trace element As, Ga, Tl, Ge, W and P by using a Mo tube, a Rh tube was used to determine Mo and an Au tube was used to determine Ag and Sb values. All XRF analyses were carried out on a Philips PW 1410 automated X-ray spectrometer with microcomputer control. The precision of the analyses is to within +/-5%.

Cold vapour AAS

Mercury could not be analysed by XRF because of interference from other elements. Samples were extracted by nitric acid, reduced by tin chloride and evolved mercury gas was analysed by atomic absorption.

Optical Emission Spectrometry

In sequence B, Hg, Sb, Pb, Ge, Th, As, Sn, Ga, In, Ag, Cd, Bi, Cu and Zn were determined as volatiles and through complete burn B, Ge, Cr, Pb, Sn, Mo, Ga, Ni, Ti, V, Co, W, Zr, Be, Nb, La, Yb, Y and Sc. Although the values obtained are only semi-quantitative the general trends discovered were essential in determining which trace elements were to be analysed for by XRF. The samples listed tables 6 and 7 were also analysed by iron flux/alumina graphite burn for Si, Al, Fe, Na, Mg, Ca, Mn, Sr, Ba, Ti, Pb, Cr, Be, V, Zr, Cu, Hg, Sb, B, Ga, W, As, P, Ge, Co and Ni but the data are not presented in this paper.

X-Ray Diffraction

Run as unoriented powders pressed on a glass slide with a thin coating of Vaseline. CuKα radiation was used, samples were run at 1°/min.

Scanning Electron Microscopy

Analysis of both chips and thin sections were conducted on a JEOL JXA-50A electron probe micro-analyser. EDAX spectra were used for the analyses.

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Table 2 Major element analyses of various Rotorua samples by XRF see table 1 for sample description

	SINTERS FROM ACTIVE ALKALINE CHLORIDE SPRINGS								FOSSIL SINTERS			OTHER SAMPLES			
SAMPLE	70205	70207	70211	70215	70217	70221	70222	70224	70232	70234	70238	70208	70218	70219	70241
SiO_2	87.67	81.37	89.02	81.38	77.87	84.72	90.57	87.26	93.95	94.45	94.07	92.02	1.32	2.47	37.3
TiO_2	-	-	0.02	0.08	0.21	0.1	0.2	0.07	0.15	0.04	-	0.61	0.05	0.05	0.13
Al_2O_3	0.18	2.96	1.54	3.82	8	3.92	0.8	0.79	0.28	0.06	0.18	0.33	9.06	13.35	5.94
Fe_2O_3	0.01	0.03	0.05	0.37	1.06	0.49	0.12	0.13	0.02	-	0.22	0.03	2.57	1.69	32.14
MnO	-	0.05	0.01	0.01	0.04	-	-	-	-	-	-	-	0.16	0.03	0.26
MgO	-	-	0.01	0.23	0.08	-	0.02	0.03	-	-	-	0.03	0.83	0.13	0.12
CaO	0.45	0.92	0.28	0.26	0.98	0.37	0.26	0.19	0.04	0.01	0.02	0.1	0.2	0.18	0.93
Na_2O	1.11	0.93	0.67	0.73	2.16	0.91	0.86	0.25	0.08	0.07	-	0.26	12.53	3.32	1.55
K_2O	0.41	0.84	0.52	0.91	0.89	0.89	0.39	0.22	0.05	0.03	0.03	0.18	1.41	0.45	1.71
P_2O_5	-	0.01	-	-	0.03	0.02	-	0.02	-	-	-	-	0.08	0.04	1.71
LOI	9.8	12.13	9.2	11.7	9.47	8.78	6.38	10.81	4.89	6.01	5.05	6.75	55.77	78.06	17.21
TOTAL	99.63	99.24	101.52	98.96	101.43	100.2	99.6	99.77	99.46	100.67	99.57	100.31	83.98	99.77	98.47

in all tables - means not detected

Table 3 Trace element analyses of the same Rotorua samples by XRF **see table 1**

	SINTERS FROM ACTIVE ALKALINE CHLORIDE SPRINGS								FOSSIL SINTERS			OTHER MINERALS			
SAMPLE	70205	70207	70211	70215	70217	70221	70222	70224	70232	70234	70238	70208	70218	70219	70241
As	28	10	17	42	35	34	51	11	5	<3	9	-	5	311	1044
Ga	213	236	172	73	19	241	117	149	42	24	<2	112	25	47	5
Ti	<3	4	9	31	<3	62	<3	<3	<3	<3	5	-	<3	5	<5
Ge	<3	<3	<3	9	6	<3	17	7	6	<3	<3	6	<3	<3	-
Ag	<2	29	276	33	<2	15	<2	6	<2	<2	<2	14	<2	<2	<2
Hg	1.35	0.71	1.57	3.42	1.39	7.07	24	-	11.9	11.6	0.23	550	46	0.14	1.36
Sb	108	25	61	63	24	36	40	36	70	10	12	120	<3	6	<3
W	14	-	4	44	-	20	-	-	55	19	<3	-	-	-	7
Mo	2	<2	2.7	<2	<2	<2	<2	-	2.1	2.1	<2	2.2	-	-	1.5
Pb	-	-	6	12	14	9	6	-	--	<3	3	-	15	5	-

Table 4 Various samples by emission spectroraphy (volatiles)

	MISCELLANEOUS SAMPLES						
SAMPLE	70210	70204	70223	70239	70240	70241	70207
B	250-350	>1000	400-500	140-180	200-250	300-400	>500
Hg	-	-	-	-	-	-	-
P	~2000	~1500	~1000	~2000	~2500	> 5000	~2000
Sb	~3000	140-180	100-150	160-200	250-300	-	50-100
Pb	80-130	40-50	30-40	120-160	100-150	5-10	50-100
Ge	15-20	10-20	-	70-90	10-156	15-20	-
Au	8-12	-	-	-	-	-	-
Tl	~1500	300-500	-	16-40	100-150	-	-
As	~ 3000	700-900	-	800-1000	~4000	>5000	-
Sn	5-7	<2	1-3	30-50	<1	1-3	<1
Ga	>1000	~400	~500	50-70	80-120	3-5	>1000
In	<1	<2	<1	<2	<1	2-4	<1
Ag	>100	>200	50-70	20-30	8-10	2-4	80-100
Cd	-	-	-	-	-	-	-
Bi	-	-	-	-	-	-	-
Cu	400-500	800-1000	250.350	200-300	80-100	30-50	200-300
Zn	100-150	120-160	400-500	200-300	300-400	100-200	-

Table 5 Same samples by emission spectroraphy (complete burn)

	MISCELLANEOUS SAMPLES						
SAMPLE	70210	70204	7023	70239	70240	70241	70207
B	150-200	>1000	250-350	150-200	100-200	250-350	>1000
Ge	10-20	<10	-	50-70	<10	10-20	-
Cr	80-120	250-350	100-150	20-30	100-150	150-200	30-40
Mn	300-400	>1000	100-150	150-200	>1000	>1000	>1000
Pb	70-90	50-60	15-25	100-150	100-150	<10-	15-25
Sn	<10	<10	<10	30-40	<10	<10	-
Mo	25-30	-	-	-	800-100	25-30	-
Ga	>100	>100	>100	40-60	5-10	<5	>100
Ni	150-200	45-60	5-10	<1	80-100	<1	<1
Ti	>1000	200-250	>1000	500-700	5-10	150-200	150-200
V	150-200	25-35	100-150	40-50	>1000	10-15	20-25
Co	<10	10-20	<10	15-20	<10	-	<10
W	350-450	130-190	100-150	<50	<50	-	<50
Zr	350-450	45-60	400-500	40-50	300-400	60-80	-
Be	2-4	50-60	6-8	4-6	3-5	>50	>50
Nb	50-70	<30	40-50	<25	<25	-	<25
La	150-250	130-150	60-80	100-150	60-80	<50	100-150
Yb	8-10	2-4	3-5	2-4	6-8	20-25	-
Y	70-90	-	-	-	40-50	100-150	-
Sc	15-25	-	-	-	-	-	-

Table 6 Miscellaneous samples analysed by emission spectrography (volatiles) **see table 1 for sample description**

	MISCELLANEOUS SAMPLES											
SAMPLE	70227	70229	70208	70213 red	70213 orange	70214	70216	70218	70219	70230	70231	70228
As	600-800	-	-	700-800	1500-1700	~7500	-	-	200-250	-	-	-
Sb	100-150	-	-	~15000	2000-2500	~5000	-	-	-	-	-	70-80
Zn	150-200	-	-	-	-	25-30	-	-	50-70	-	-	150-200
Tl	150-250	5-10	-	150-200	40-60	25-35	-	-	-	-	<5	200-250
P	500?	1000?	1000?	100-150	3000-4000	-	?	500-700	-	?	?	-
Cu	100-150	40-50	50-60	100-150	800-1000	400-600	40-60	70-90	70-80	50-60	70-90	100-150
Ga	70-80	300-500	150-200	150-250	150-200	60-75	100-150	3-5	70-80	50-60	60-70	70-90
Ag	20-25	20-75	40-50	>7500	700-800	700-800	3-5	<1	<1	4-6	15-25	6-8
B	15-20	400-500	250-300	50-70	200-250	45-60	400-500	2-4	-	70-90	200-250	10-15
Pb	-	-	-	50-70	-	25-30	-	-	-	-	-	10-15
Au	-	-	-	15-20	-	-	-	-	-	-	-	-
Ge	-	-	-	<7.5	-	10-15	-	-	-	-	-	-
Sn	-	-	-	-	-	2-3	-	-	5?	-	-	-
In	-	-	<1	-	-	<1.5	-	1-2?	-	-	-	1?

Table 7 The same miscellaneous samples shown in table 6. Results of complete burn emission spectrographic analysis

	MISCELLANEOUS SAMPLES									
SAMPLE	70227	70229	70208	70216	70220	70218	70219	70230	70231	70228
Mn	500 - 600	40 - 60	10 - 15	20 - 30	150 - 200	700 - 800	300 - 400	15 - 20	15 - 25	400 - 600
Ti	800 - 1000	100 - 150	>1000	100 - 150	>1000	90 - 110	350 - 450	>1000	350 - 450	150 - 250
Zr	150 - 250	-	400 - 500	15 - 20	400 - 500	15 - 25	30 - 50	300 - 350	-	-
Cr	150 - 200	15 - 25	10 - 20	100 - 150	40 - 50	80 - 100	150 - 250	150 - 200	<10	25 - 35
W	-	<50	250 - 450	<50	80 - 120	<50	-	250 - 350	<50	-
Co	-	-	25 - 35	-	-	-	30 - 50	5 - 10	-	-
V	15 - 20	-	10 - 15	5 - 10	70 - 90	50 - 60	50 - 80	10 - 20	-	5 - 10
Ni	20 - 25	-	<5	3 - 5	<5	8 - 10	25 - 30	30 - 40	<5	<5
Pb	10 - 15		-	-	20 - 30	-	-	-	-	10 - 20
Mo	3 - 5	<1	<1	<1	<1	3 - 5	5 - 10	5 - 7	<1	<1
Sn	-	-	-	-	-	-	-	5 - 8	-	-
Be	6 - 7	12 - 16	5 - 10	10 - 15	10 - 15	1 - 2	-	3- 4	3 - 4	5 - 10
Yb	1 - 2	-	1 - 2	<1	2 - 4	3 - 5	2 - 3	2 - 3	-	<1
Y	-	-	-	-	25 - 30	35 - 45	-	-	-	-
Ge	-	-	-	-	-	-	-	-	-	-