TRACE ELEMENTS IN AUSTRALIAN OPALS USING NEUTRON ACTIVATION ANALYSIS

G.D. McORIST*, A. SMALLWOOD**, J.J. FARDY*

* *ANSTO Environmental Science Program,*
Lucas Heights Research Laboratories,
Private Mail Bag 1, Menai, NSW, Australia.

** *Lecturer, Gemmological Association of Australia,*
24 Wentworth Ave, Sydney, NSW, Australia.

Neutron activation analysis was used to determine the concentration of trace elements in 42 samples of black, grey and white opals taken from a number of recognised Australian fields. The results were evaluated to determine if a relationship existed between trace element content and opal colour.

Introduction

Opal is a form of silica chemically similar to quartz, but containing a variable amount of water within the mineral structure[1]. It has a composition of $SiO_2.nH_2O$. There are two basic types of opal. "Precious" opal is composed of small spheres of amorphous silica arranged in a regular pattern: these form a three-dimensional diffraction grating which is responsible for what is commonly termed, a play of colours. "Common or potch" opal, on the other hand, varies from transparent to opaque but does not exhibit the play of colour since their silica spheres differ in size, shape and packing order.

Common opal can be found in a large number of countries around the world but has no commercial value. However, precious opal is only found in a few scattered deposits. Overseas deposits of opal are predominantly in volcanic host rocks. The Australian deposits of precious opal are distinctive because the associated host rocks are not volcanic but sedimentary[2]. Australian production of precious opal has now dominated the world market for some time with the main fields located at Lightning Ridge in NSW and Coober Pedy and Andamooka in South Australia (Figure 1).

Most opals found in Australia are either black, grey, white or transparent. Opals can also be yellow, red, green, blue or pink in colour but are less common than those described above. Opals, like other gemstones, can be made synthetically. Briefly, this involves the chemical production of correct sized silica spheres in the laboratory and their settling into a gel which, when cured, gives rise to the synthetic opal.

Although a number of researchers have studied the formation, structure and properties of opals[4-8], few workers have actually determined their trace element content[9,10]. Similarly, a number of analytical methods have been used to determine trace elements in silicates[11,12], but they have not been used to analyse opals. Neutron activation analysis (NAA) is uniquely suited to this type of sample for a number of reasons. Firstly, the opal matrix is mainly silica which is poorly activated when exposed to neutrons. For this reason, the concentration of many elements in the sub-ppm range can be determined. Secondly, NAA is a non-destructive technique which is particularly useful when analysing valuable materials such as precious opals. Thirdly, a sample may be sub-divided after analysis to establish possible differences in trace element content between the precious and common sections.

The purpose of this work is to use NAA to analyse opals from a number of recognised fields in NSW and South Australia in order to characterise the trace element content of Australian opals and to determine if a relationship exists between trace element content and opal colour. In order to simplify interpretation of data, this study was restricted to common (or potch) black, grey and white Australian opals.

Experimental

Opal Preparation

Samples of white (light), black (dark) and grey opal were obtained from a number of recognised opal fields in NSW and South Australia. The black and white colours are also known, within the opal industry, as dark and light, respectively. Opal was cut from the surrounding, rough material using a 10 inch diamond-impregnated steel lapidary saw which was cooled by tap water. A number of smaller sub-samples were then cut from these and thoroughly washed (detergent/water) to remove any extraneous contamination. Resulting opal samples were dried, weighed and individually placed into pre-cleaned (8M nitric acid, high-purity demineralised water and A.R. ethanol) polythene irradiation containers.

Sample Irradiation

Multielemental standards were prepared by accurately weighing about 100 mg of NBS F1633A fly ash into pre-cleaned polythene containers.

Samples and standards were irradiated in the X-176, self-service, pneumatic tube of the Australian Nuclear Science and Technology Organisation's 10 MW reactor, HIFAR, for 1 minute at a thermal flux of 2.5 x 10^{13} n cm^{-2} sec^{-1}. After 20 minutes decay, they were counted for 10 minutes using an 18% Ortec HPGe detector coupled to a Series 40 Canberra multichannel analyser. Each sample and standard was also recounted (45 minutes each) after 24 hours decay. The resulting data were processed by Fortran programmes developed by members of our group.

The same samples and standards were re-irradiated in the X-6 tube of HIFAR for 18 hours at a thermal flux of 5 x 10^{12} n cm^{-2} sec^{-1}. After 7 and 28 days, they were counted for 2 and 4 hours, respectively, using a sample changer system attached to another 18% Ortec HPGe detector also coupled to a Series 40 Canberra multichannel analyser. Data were processed by Fortran programmes as before, providing results for more than 30 elements on 48 white, black and grey opals.

Results and Discussion

A similar number of white, black and grey samples from fields in both NSW and South Australia were sought. However, this was difficult since black and grey opals are common in Lightning Ridge in NSW but white samples are rare. The converse occurs in South Australia. A total of 42 samples of common Australian opal were analysed using NAA. Nine black, 3 white and 6 grey opals were taken from fields at Lightning Ridge in NSW with a further 6 black and 18 white opals originating in South Australia (Coober Pedy, Mintabie and Lambina). The results for the analysis of these samples are summarised in Tables 1 - 3. Figures 2 - 12 compare the concentration for individual elements for each group of opals.

The mean concentration of the 23 elements found in NSW white opals were similar, in all cases, to those of South Australian white opals (Table 1). In most cases, the concentration range for the NSW samples fell within those for the South Australian samples, mainly since more samples were analysed for the latter. The exceptions were Mn, Fe and Ba where, although overlap did not occur, the results were within a factor of three in all cases.

Figures 2 - 12 show results for some of the elements found in the 21 white opals analysed. Groups 3 and 4 represent individual results for the 3 NSW and 18 South Australian white (light) opals, respectively. The figures confirm that the variation in concentration of individual elements in white opals is very small, regardless of origin.

In contrast, the trace element content of black opals from NSW was noticeably different to those originating in South Australia (Table 2). In the case of NSW black opals, the concentrations of 34 elements were determined compared with only 24 for the South Australian variety. Although mean results for some elements such as Na, Mg, Al, K, Ca, Mn, Fe, Rb, Sr, Cs, Ba, Hf and Ta were similar, all other results were significantly higher for black opals from NSW when compared with the same coloured opals from South Australia. These variations are more clearly seen in Figures 2 - 12. Groups 1 and 2 show individual analysis results for the nine NSW and six South Australian black (dark) opals, respectively. Although the NSW samples were taken from three different areas within close proximity, large and inconsistent variations were still observed.

Surprisingly, the mean and range of results for South Australian *black* opals are almost identical to *white* opals from similar locations in the same state. This is more clearly seen for those elements represented in Figures 2 - 12, where groups 2 and 4 are the results for black (dark) and white (light) samples, respectively. This data indicates that a relationship between trace element content and opal colour appears unlikely. The similarity of the South Australian results implies that the trace element content of an opal is more likely to be related to that of the surrounding rock matrix.

Only grey opal samples from Lightning Ridge in NSW were analysed for trace elements. Since grey opals could be considered a type of "light black" opal, it is not surprising that the mean results for all trace elements common to both black and grey NSW opals were similar. The only differences were for Cl which was clearly present only in some grey opals and Au which was found only in some black opals. Once again, Figures 2 - 12 more clearly show these associations. The range of results for Sc, Ti, V, Cr, As and the rare earths are similar whereas the results for the other elements are more closely grouped around the mean in the grey samples.

Conclusions

This investigation determined the trace element profile of 42 common opals from a number of recognised fields in NSW and South Australia. Elemental results for white opals were similar in all cases regardless of sample origin. Although the concentration of some elements found in black opals from NSW were similar to those from South Australia, the remainder showed significant differences. The noticeably higher results for NSW black opals more closely mirrored results for grey opals from the same state. As far as common opals are concerned, no definite relationship could be established relating trace element content to opal colour.

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Table 1

Trace element concentration ranges and means in white opals from NSW and South Australia (ug g^{-1})

Element	New South Wales				South Australia			
	Range			Mean	Range			Mean
Na	930	-	1400	1090	280	-	1700	820
Mg	290	-	430	350	160	-	290	190
Al	6500	-	9500	7700	6000	-	10000	7100
K	1100	-	1700	1350	1000	-	3000	1900
Ca	1600	-	2600	2000	670	-	3100	1800
Sc	0.37	-	0.53	0.43	0.04	-	0.40	0.22
Mn	16	-	24	19	4.2	-	14	8.1
Fe	710	-	1000	810	150	-	620	450
Co	0.10	-	0.30	0.23	0.10	-	0.51	0.22
Rb	11	-	17	13	11	-	23	18
Sr	40	-	60	50	19	-	200	97
Sb	0.1	-	0.1	0.1	0.04	-	1.70	0.38
Cs	2.3	-	3.3	2.6	1.8	-	4.7	3.3
Ba	80	-	110	93	140	-	490	310
La	0.5	-	0.8	0.7	0.5	-	3.1	1.4
Ce	0.9	-	1.5	1.3	0.8	-	6.5	2.6
Sm	0.08	-	0.15	0.11	0.04	-	0.48	0.17
Eu	0.03	-	0.04	0.04	0.01	-	0.15	0.05
Dy	0.1	-	0.1	0.1	0.04	-	0.30	0.13
Yb	0.03	-	0.06	0.05	0.01	-	0.18	0.07
Hf	7.7	-	10.9	8.8	1.8	-	8.4	5.0
Ta	0.07	-	0.13	0.10	0.04	-	0.40	0.21
Th	0.2	-	0.4	0.3	0.05	-	1.70	0.47

Table 2

Trace element concentration ranges and means in black opals from NSW and South Australia (ug g^{-1})

Element	New South Wales		South Australia	
	Range	Mean	Range	Mean
Na	700 - 1800	1000	270 - 530	410
Mg	170 - 320	260	140 - 250	210
Al	5900 - 10200	7700	5800 - 7500	6500
K	920 - 4000	2400	1700 - 2100	1900
Ca	1300 - 2700	2000	700 - 2200	1400
Sc	0.6 - 5.2	1.7	0.06 - 0.18	0.11
Ti	120 - 1900	720		< 42
V	1.7 - 15	6.2		< 0.5
Cr	1.1 - 7.0	2.8		< 0.5
Mn	16 - 38	26	8.3 - 9.8	9.1
Fe	810 - 2000	1200	200 - 590	380
Co	7 - 120	39	0.07 - 0.38	0.23
Cu	36 - 1100	280		< 21
Zn	6 - 130	30		n.d.[1]
As	2 - 26	9.8		< 0.7
Rb	8 - 20	14	18 - 21	20
Sr	30 - 80	52	31 - 86	57
Sb	0.4 - 6.6	2.1	0.03 - 1.1	0.23
Cs	2.4 - 3.0	2.6	2.3 - 3.6	2.9
Ba	100 - 190	140	120 - 350	240
La	4 - 60	19	0.86 - 2.0	1.5
Ce	10 - 91	35	2.0 - 2.9	2.5
Nd	4 - 39	15		< 1.9
Sm	0.9 - 11	3.7	0.10 - 0.15	0.13
Eu	0.3 - 2.1	0.9	0.03 - 0.06	0.05
Tb	0.1 - 0.9	0.4		< 0.04
Dy	0.5 - 4.8	2.0	0.06 - 0.90	0.25

Table 2 (cont.)

Trace element concentration ranges and means in black opals from NSW and South Australia (ug g^{-1})

Element	New South Wales		South Australia	
	Range	Mean	Range	Mean
Yb	0.3 - 3.4	1.2	0.02 - 0.14	0.08
Lu	0.05 - 0.50	0.19	0.01 - 0.02	0.01
Hf	3.3 - 17	8.1	2.9 - 6.6	4.6
Ta	0.16 - 0.70	0.34	0.13 - 0.34	0.21
Au	0.005 - 1.4	0.26		< 0.001
Th	2.0 - 25	8.1	0.18 - 0.43	0.31
U	0.6 - 6.6	2.3		< 0.2

Notes: 1. Not detected. Computer program could not provide a "less than" result due to spectral interference.

Table 3

Trace element concentration ranges and means in grey opals from NSW (ug g^{-1})

Element	New South Wales			
	Range			Mean
Na	990	-	3100	2000
Mg	240	-	340	290
Al	7400	-	11800	9400
Cl	< 16	-	95	52
K	650	-	3400	2500
Ca	1700	-	2600	2100
Sc	1.5	-	2.4	1.7
Ti	370	-	1700	760
V	3.5	-	13	6.7
Cr	1.1	-	4.0	2.1
Mn	22	-	29	25
Fe	800	-	1200	1000
Co	3	-	35	20
Cu	58	-	150	110
Zn	4	-	27	16
As	4	-	18	9
Rb	6	-	17	12
Sr	64	-	110	78
Sb	0.5	-	1.1	0.8
Cs	3.0	-	4.1	3.6
Ba	190	-	380	230
La	13	-	41	23
Ce	25	-	77	45
Nd	11	-	29	18
Sm	2.2	-	6.7	3.9
Eu	0.7	-	2.0	1.1
Tb	0.3	-	0.9	0.5

Table 3 (cont.)

Trace element concentration ranges and means in grey opals from NSW (ug g^{-1})

Element	New South Wales			
	Range			Mean
Dy	1.7	-	4.2	2.5
Yb	1.1	-	3.5	1.7
Lu	0.2	-	0.5	0.3
Hf	0.9	-	11	8.0
Ta	0.3	-	0.6	0.4
Th	5.5	-	11	7.5
U	1.7	-	3.0	2.0

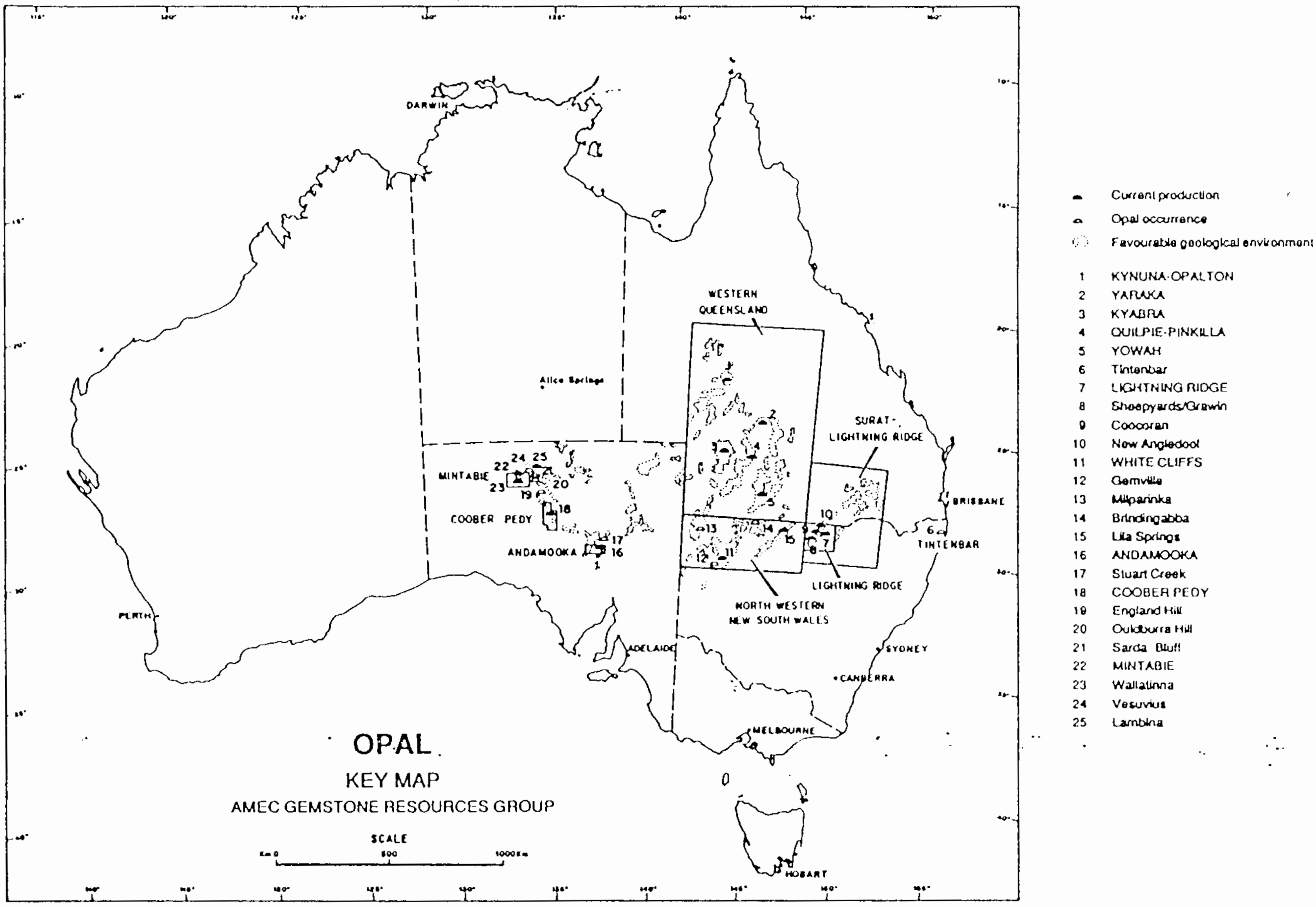

Fig 1: Location of opal fields in Australia[3]

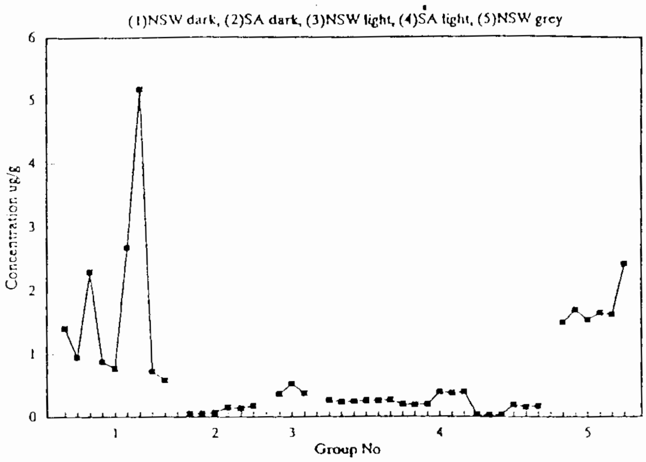

Fig 2: Sc content of opals

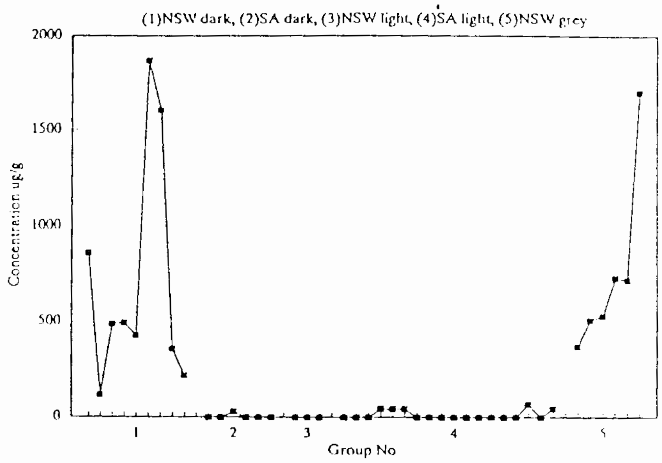

Fig 3: Ti content of opals

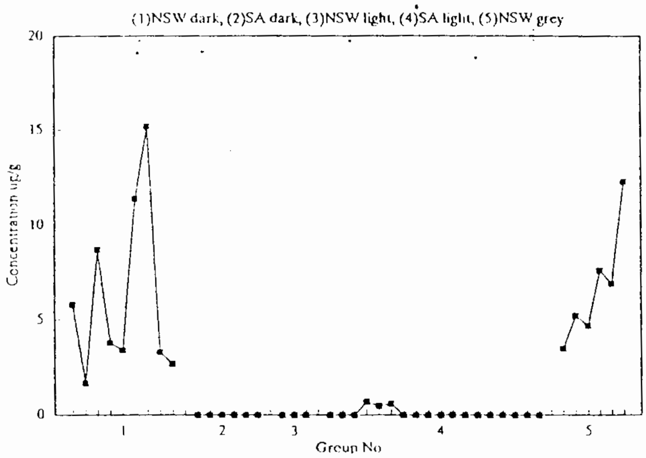

Fig 4: V content of opals

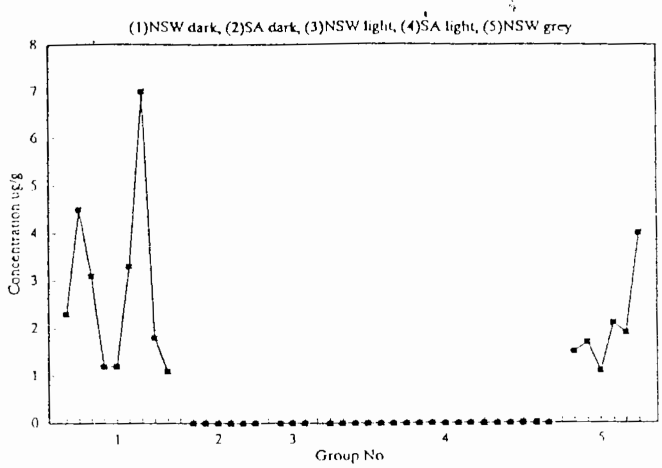

Fig 5: Cr content of opals

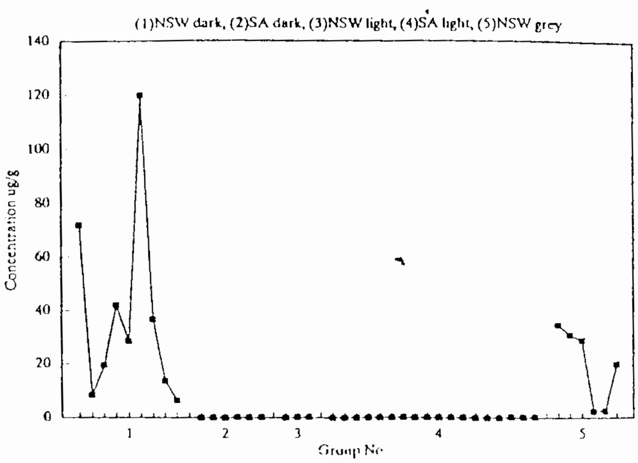

Fig 6: Co content of opals

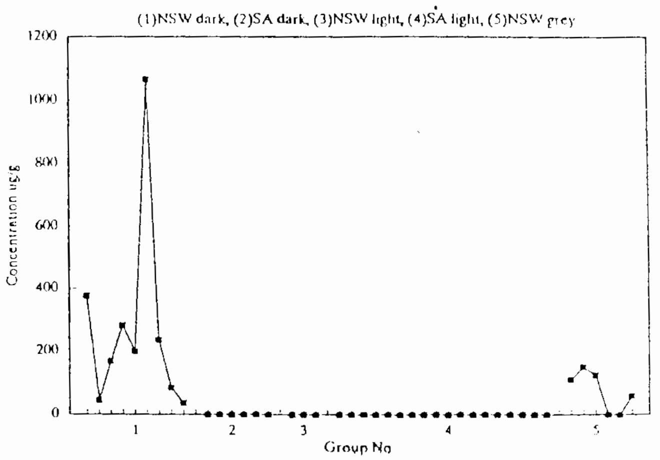

Fig 7: Cu content of opals

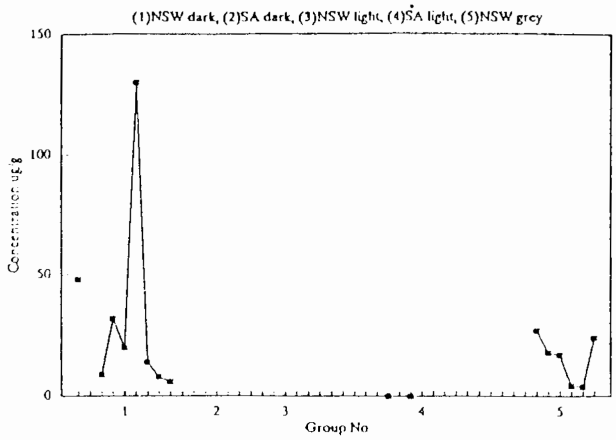

Fig 8: Zn content of opals

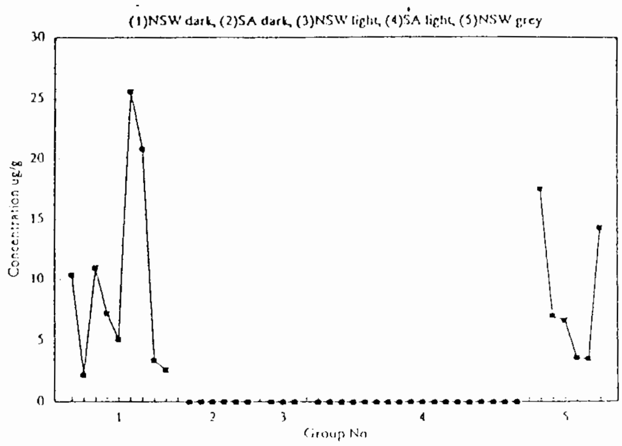

Fig 9: As content of opals

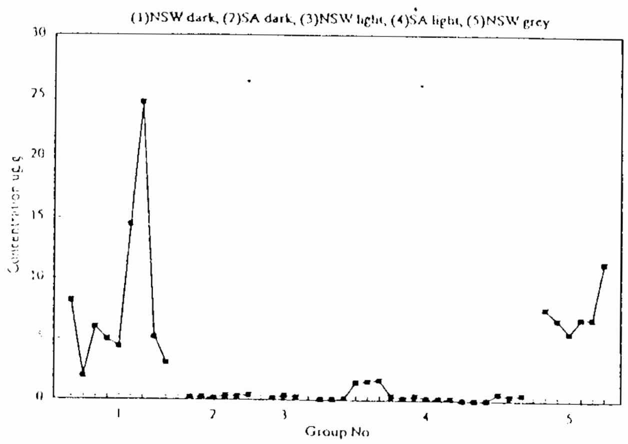

Fig 10: Th content of opals

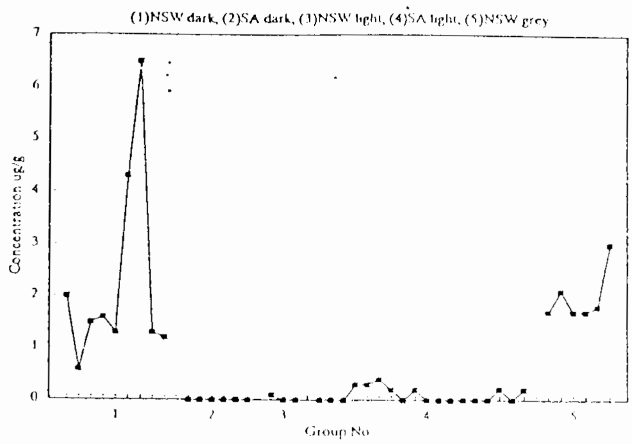

Fig 11: U content of opals

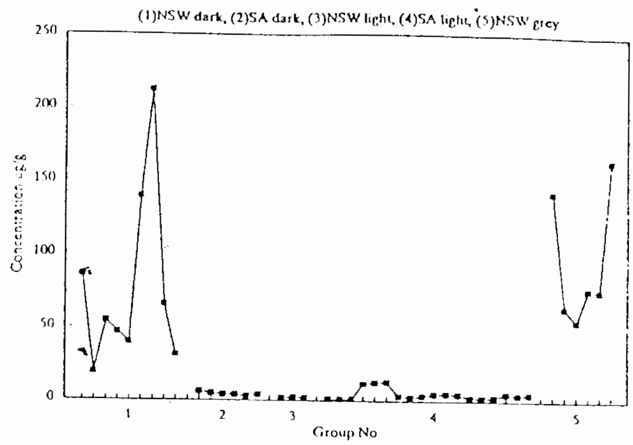

Fig 12: Rare earths content of opals