GEOCHEMICAL DISPERSION OF ELEMENTS IN BYROCK-HERMIDALE GROUNDWATERS, COBAR REGION NSW

Kamal Khider

CRC LEME, Department of Earth and Marine Sciences, ANU, ACT, 0200

INTRODUCTION

Exploration indicators (pathfinders) in groundwater are produced by the chemical reactivity of water with soil, regolith and covered rocks during its lateral and vertical movements. Therefore, chemical analysis of groundwater will assist in understanding controls on element dispersion. Water samples from seventeen boreholes in the Byrock-Hermidale region have been analysed by the Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) method. Sampled boreholes were prefixed with "CBAC" and included numbers 150, 154, 158, 160 and 173 from Hermidale region and 238, 218, 219, 243, 242, 248, 217, 227 and 231 from Byrock region (Figure1).
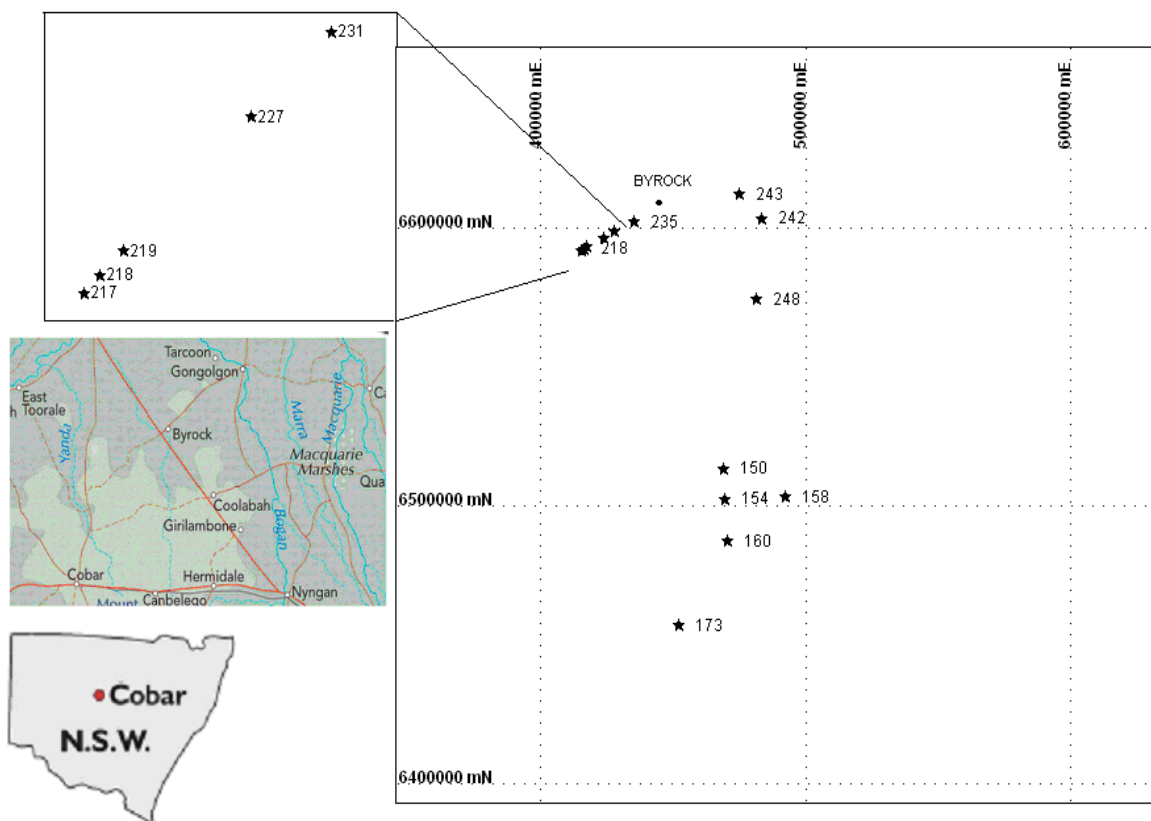

Figure 1: Location map and borehole locations.

GEOLOGICAL BACKGROUND

The predominant components of the aquifers for the sampled boreholes (150, 154, 160, 173, 218, 227, 231, 235, 243, 248) are weathered (saprolite and saprock) clastic rock materials, sandy phyllites, quartz veins and volcaniclastics. Transported materials were the main aquifers in 158 and 242. Mafic volcanic rocks were recognised from 217 and 235. The depth to groundwater varies from relatively shallow (11.8-47.3 m) in the Byrock area to relatively deep (18-65 m) in the Hermidale area.

pH AND METAL CONCENTRATION

Many processes in natural water are either dependent on, or alternately are manifested by, some change in the hydronium ion (H_3O, H^+) concentration (measured as pH). The solubility of most metallic elements and the stability of their compounds is sensitive to the pH of the aqueous environment and they tend to precipitate as hydroxides.

The pH values in the water samples are generally near neutral, the median pH at Byrock near 6.85 and at

Hermidale 7.15 (Table 1). The total range of pH is from 6.43 in 160 to 7.24 in 242. There is no clear correlation between pH and the depth of the watertable (Figure 2). This may reflect the effective mineral neutralisation that occurs when rain comes into contact with the soil, regolith and finally bedrock.

The relationship between the pH and the concentrations of Cu and Zn in both the Byrock and Hermidale areas generally shows concurrent comparative change in Cu and Zn concentrations in all studied sites except 217, where the Cu concentration is 0.33 mg/l. The minimum content of Cu and Zn is above 0.01 mg/l (Figure 3). This level of Cu and Zn concentration for the measured pH matches that typical of water from sites of mineralisation at Mt Isa and Broken Hill (Giblin 2001). This suggests that the water has been in contact with Cu and Zn mineralisation.

Table 1: Statistics of EC, pH, Eh, Temperature and Alkalinity of Byrock A and Hermidale B areas.

A Parameters	Quartiles	EC μS/cm	PH	EH	Temp°C	Alk. mg/l
Median		14,960	6.86	350	22.3	543.90
Range		18,069	.76	102	2.4	507.20
Minimum		891	6.51	305	21.6	294.00
Maximum		18,960	7.27	407	24.0	801.20
Percentiles	25	4,708	6.61	342	21.8	404.23
	50	14,960	6.86	350	22.3	543.90
	75	16,755	7.16	368	23.4	643.13

B Parameters	Quartiles	EC μS/cm	PH	EH	Temp°C	Alk. mg/l
Median		20,100	6.89		26.0	247.45
Range		24,400	.69		4.0	298.90
Minimum		7,200	6.43		23.0	196.00
Maximum		31,600	7.12		27.0	494.90
Percentiles	25	10,740	6.46		23.5	218.05
	50	20,100	6.89		26.0	247.45
	75	29,400	7.02		27.0	490.00
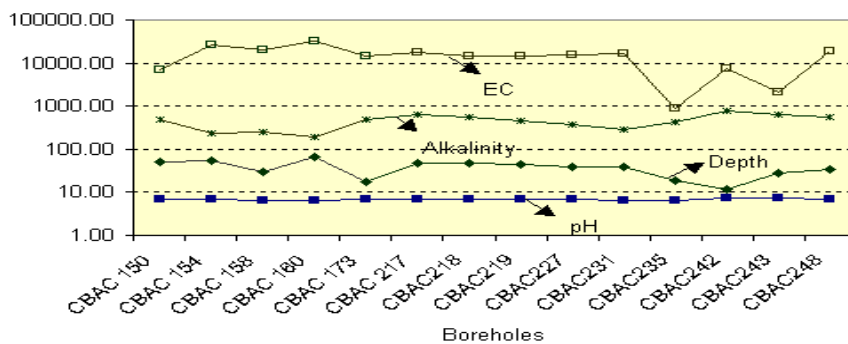
Figure 2: Ground water pH, depth, alkalinity, and Electrical conductivity (Ec) in Byrock and Hermidale areas.
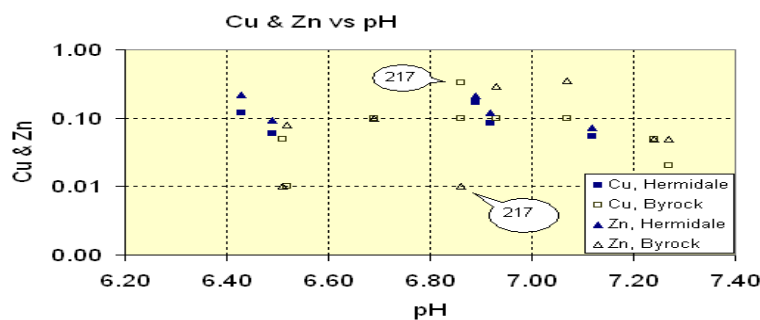
Figure 3: Cu and Zn relationship with pH in the studied water samples.
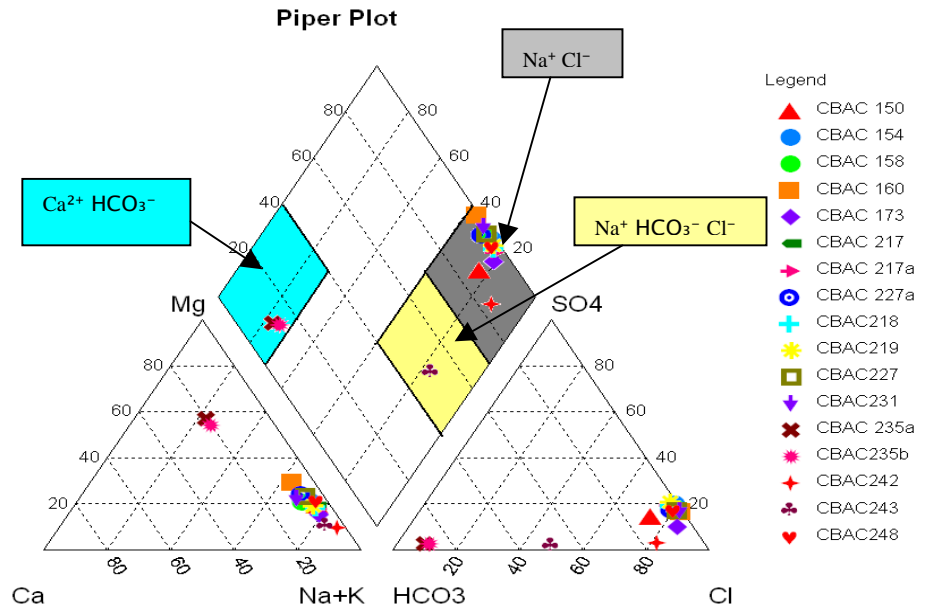
GROUNDWATER TYPES

The studied groundwaters in the Byrock-Hermidale region can be classified into three main types (Figure 4):

1. Chloride type, where the anion is chloride and the cation is mainly sodium or potassium. This type of water occurs in almost all the studied sites except 235 and 243 (Figure 4). The EC measurements showed that the majority of the waters are over 5,000 μS/cm level of conductivity (Figure 2) and this is mostly related to the predominant occurrence of sodium chloride;

2. Calcium-bicarbonate type. This groundwater type is rich in Ca^{2+} Mg^{2+} and HCO_3^{-}, and the effect of salinity is minimal. The high concentration of calcium and magnesium may indicate predominant

weathering of Ca-Mg bearing host rocks (White *et al.* 1963). Calcium-bicarbonate type groundwater was only reported from 235; and,

3. Bicarbonate-chloride type. This type of water occurs in 243 and includes moderate amounts of HCO_3^{3-}, Cl^- and Na^+.

Figure 4: Piper plots illustrating different types of groundwater in the study area


ROCK-GROUNDWATER INTERACTIONS

The effect of the mineral-water interaction near the landscape surface is reflected in EC values. At the Byrock sites, median EC is near 1,500 µS/cm and less than 1,000 µS/cm in shallow boreholes 235, 242 and 243. The relatively high EC at 242 is mostly a result of mixing with higher EC water. The EC increased to 15,000-19,000 µS/cm in deeper boreholes. This is consistent with evaporative concentration and the possibility that the deeper groundwater has been in contact and interacting with weathering minerals longer (Caritat *et al.* 1998). The pattern between the EC and water depth shows similar correlation in the Hermidale area (Figure 2).
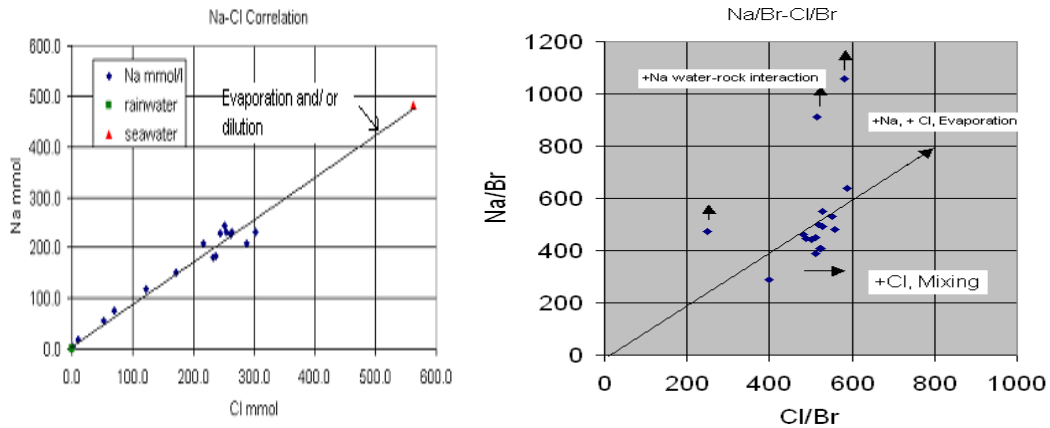

Figure 5a (left): Na-Cl and **b (right)** Cl/Br and Na/Br correlations indicating compositional trends consistent with rainwater evaporation and/or seawater dilution, mixing and water-rock interaction for Byrock-Hermidale waters.

The Na-Cl and Na/Br-Cl/Br relationships of Byrock and Hermidale groundwater (Figure 5a, b) illustrates that both waters lie on the seawater dilution line and/ or rainwater evaporation trend, with some excess of Na (cation exchange or albite dissolution) and Cl. This means that waters are enriched in Na and Cl to various degrees, presumably because of evaporation and variable mixing of rainwater. The concentrations of Ca and SO_4 in shallow water sites in the Byrock area (e.g., 235, 242 and 243) and in the deeper boreholes 231, as well as 158, 160 and 173 from the Hermidale area (Table 2) are higher than the seawater dilution trend (Figure 6). The elevated Ca concentration can be related to the leaching of carbonate minerals by water -rock interaction and the mobilisation of Ca due to cation exchange in the soil and regolith. Water compositions at

least two sites (150 and 227; Figure 6) approximately represent seawater dilution, which suggests concentration by evaporation or dissolution of gypsum. All the other sites show enrichment in SO_4 relative to Ca, which may relate to precipitation of Ca as carbonate and/or oxidation of sulphides. Increasing SO_4, Ca and Cl contents (Figure 7a) support mixing with higher salinity water. High cation (Ca^{2+}, Fe^{2+}, Mg^{2+}) concentration can be mainly attributed to weathering of basic silicates; which may be accelerated under extreme SO_2 loading (Caritat *et al.* 1998). The relationship between K+Na and Ca+Mg (Figure 7b) suggests a predominant felsic component in nearly all the studied sites, except 235. Water in the latter has more likely been in contact with mafic rocks, and this is consisted with the occurrence of basalt in the aquifer (Glanville *et al.* 2003).
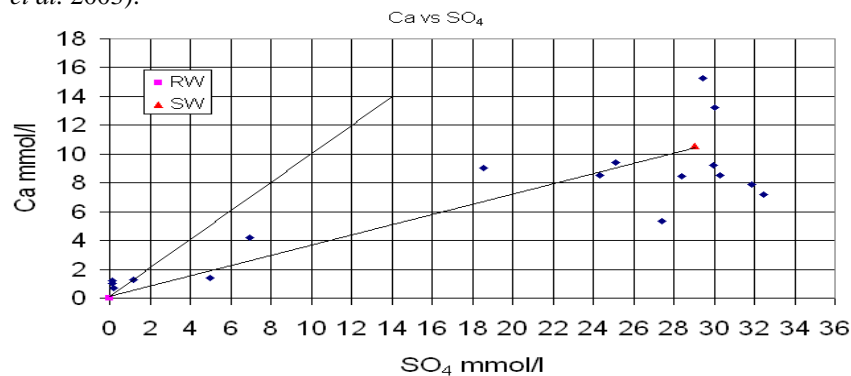
Figure 6: Ca- SO_4 relationships with rainwater evaporation and/or sea-water dilution, and Ca:SO_4 1:1 ratio lines of Byrock-Hermidale groundwater.
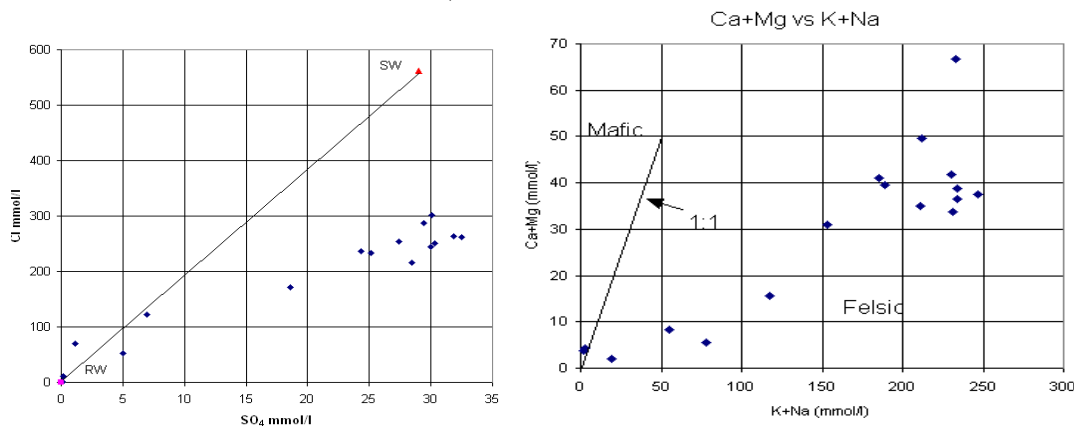
Figure 7a (left) and b (right): The SO_4 relationships with Cl and rainwater (RW) evaporation-seawater (SW) dilution line (**a**), and relationship between K+Na and Ca+Mg and type of aquifer rock (**b**).

## CLUSTER ANALYSIS AND GEOCHEMICAL ASSOCIATIONS

Cluster analysis (Word's method) was used to group variables, in this case geochemical measurements (field parameters, cations and anions concentrations) after transforming the data using natural log transformation. Data were excluded from any variable where more than 20% of the values were below the detection limit. The variables dendrogram (Figure 8) shows four associations of geochemical parameters at Similarity Distance Level (SDL) near 7.5. These are:

Table 2: Water depth (DWT), EC and concentration of SO_4 and Ca in the studied boreholes.

ID	DWT M	EC uS.cm-1	SO4 mg/L	Ca mg/L
CBAC 150	50	7200	480	56
CBAC 154	55	27200	2877	369
CBAC 158	30	20100	1782	362
CBAC 160	65	31600	2888	531
CBAC 173	18	14280	669	168
CBAC 217	47.3	17390	3060	316
CBAC218	46.22	14820	2910	341
CBAC219	43.4	14960	2730	340
CBAC227	39.23	15220	2340	342
CBAC231	38.6	16120	2830	613
CBAC235	18.6	891	9.76	47.3
CBAC242	11.8	7240	112	50.9
CBAC243	28	2176	19.2	28.2
CBAC248	34	18960	2630	215

1. Cl-Na-Br-EC-SO_4-Cu Group. This group can also be called a salinity group because it includes EC and all its constituents (except Cu) virtually represent the main salinity products (e.g., Na, Cl, SO_4 and Ba). Not all the members of this group have the same level of similarity. Na, Ba and Cl are the closest subgroup clustered at similarity distance level (SDL) 1, and they combine with EC and SO_4 at SDL 2. All the members clustered as a group at SDL 3 with Cu. This relationship simply means that the first three elements mostly represent chloride related to salinity. The absence of associated Ca suggests that SO_4 is not related to gypsum or anhydrite. The clustering discloses the close relationship of SO_4 with Cu (Figure 9), and this may be related to occurrence of Cu as sulfide minerals. It also explains the effect of SO_4 as a complexing agent on controlling solubility of Cu in this environment.

2. Ca-Sr-Mg-K group. This group consists a Ca-Sr and Mg subgroup clustered in SDL 1. These elements further group with K in near SDL 5(Figure 8). The subgroup of Ca-Sr and Mg represents the weathering products of carbonate, clay and mafic igneous rocks (Taylor & Eggleton 2001). The absence of alkalinity (generally considered an index of carbonate activity) from the Ca-Mg assemblage can be used as evidence to limit carbonate contribution as an explanation for this subgroup. The occurrence of K in this group is further evidence for the weathering of igneous and metamorphic rocks as the control for enrichment of these elements in the studied groundwater.

3. pH-Alkalinity group. pH and alkalinity cluster as a subgroup at SDL 4. This relationship can be explained as a result of the interaction between water and surrounding minerals that commonly consume acid and yield free cations and higher alkalinity. This results in progressively higher pH (Drever 1997).

4. Si-Zn-Ba-Group. Although Si, Zn and Ba are not strongly linked, their relationship with pH and alkalinity shows that these variables have some effect on Si and Zn concentrations. The pH in the studied samples is almost neutral to very slight acid, which may only slightly be able to adjust the dissolution of Zn and Si. Barium is nearly independent and grouped in SDL 7.5.
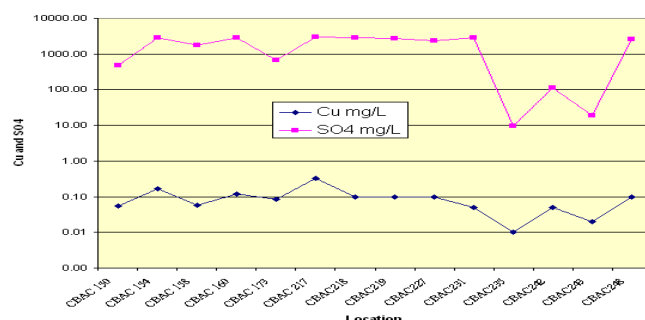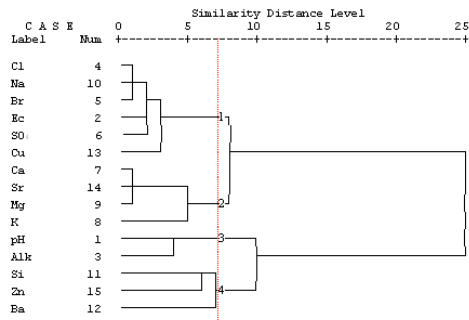
Figure 8: Cluster analysis dendrogram for analysed variables in the Byrock-Hermidale waters showing four main clusters at SDL 7.5.


Figure 9: Distributions of Cu and SO_4 in the groundwaters of Byrock-Hermidale region.

GEOGRAPHIC DISTRIBUTION

Cluster analysis can also be used to gather the borehole locations into small groups based on the geochemical similarities of their waters. On SDL 5 the studied boreholes can be collected in five groups (Figure 10) as follow:

I.   219-248-154-160;
II. 217-227-218-231;
III. 158-173;
IV. 150-242-243; and,
V.   235.
VI.

All the recognized location groups are characterized by a high percentage of G1 (Cl, Na, Br, Ec, SO4, Cu) ranging from 96.69 at 160 to 60.03 at 235 (Table 3). GI and GII consist of a homogenous mixture of cluster group G2 and G3 with significantly less concentrations of G4. GIII and GIV show gradual increasing in G3 and G4. GV characterized by elevated occurrence of G2, G3 and G4 with relatively low G1 (Figure 11).
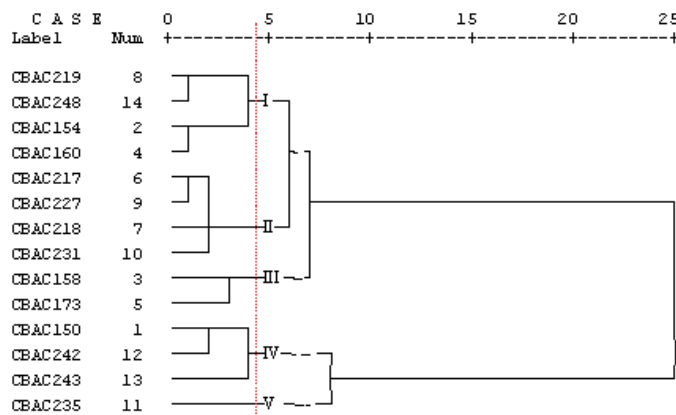
Figure 10: Cluster analysis dendrogram showing the grouping of studied locations of groundwater in Byrock-Hermidale area.
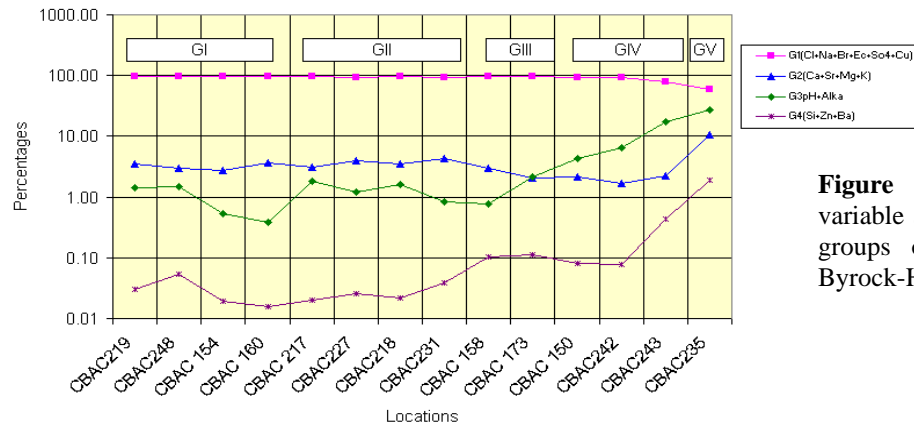
Figure 11: Distribution of variable association and location groups of cluster analysis of Byrock-Hermidale groundwater.

CONCLUSIONS

Groundwater is an important potential sampling medium for geochemical exploration. Groundwater chemistry can reflect changes in country rock, alteration and interaction of groundwater with a body of mineralisation. A chemical study of groundwater was carried out to elucidate processes controlling water type and secondary dispersion of elements in selected sites from the Byrock-Hermidale region. ICP-OES, analysis showed that the water in the region is mainly of Chloride type, rich in Na, Cl and SO_4 .The other Calcium-bicarbonate and Bicarbonate – chloride types are not predominant. Variations of metal concentration with pH showed significant enrichment (> 0.01 mg/l) of Cu and Zn. The high Ca concentration suggests leaching of Ca-minerals by water -rock interaction and the mobilisation of Ca in the soil and regolith. The relationship between Ca and SO_4 in 150 and 227 coincides with seawater dilution, which indicates evaporation or dissolution of gypsum.

Table 3: Occurrences of variable groups (clusters) for groundwater cluster analysis of the studied boreholes in Byrock-Hermidale area.

	G1 (Cl+Na+Br+EC+SO4+Cu)%	G2 (Ca+Sr+Mg+K)%	G3 (pH+Alk.)%	G4 (Si+Zn+Ba)%
219	95.03	3.51	1.43	0.03
248	95.50	2.95	1.50	0.05
154	96.69	2.75	0.54	0.02
160	95.89	3.71	0.38	0.02
217	95.06	3.13	1.79	0.02
227	94.80	3.98	1.19	0.03
218	94.83	3.53	1.62	0.02
231	94.77	4.36	0.84	0.04
158	96.15	2.97	0.78	0.10
173	95.72	2.02	2.14	0.11
150	93.39	2.18	4.34	0.08
242	91.84	1.68	6.41	0.08
243	80.13	2.25	17.85	0.44
235	60.03	10.70	27.39	1.88

All the other sites 158, 160 and 173 from Hermidale region and 238, 218, 219, 243, 242, 248, 217 and 231 from the Byrock region show more enrichment in SO_4 than Ca, which may relate to precipitation of Ca and/or oxidation of sulphides. The association of this enrichment with increasing Cl content supports a mixing process. Cluster analysis effectively highlights certain elemental and location associations that are difficult to deduce by means of more conventional methods.

REFERENCES

CARITAT P. DE, DANILOVA S., JAEGER Ø., REIMANN C. & STORRØ G. 1998. Groundwater composition near the nickel-copper smelting industry on the Kola Peninsula, central Barents Region (NW Russia and NE Norway). *Journal of Hydrology* **208**, 92-107.

DREVER J.I. 1997. *The geochemistry of natural waters: surface and groundwater environments*, 3rd ed. Prentice-Hall Inc., New Jersey.

GIBLIN A.M. 2001.*Groundwaters, geochemical pathfinders to concealed ore deposits*. CSIRO, 70p.

GLANVILLE D.H., ROACH I.C. & MCQUEEN K.G. 2003. Regolith-landform mapping, leucitite basalt and the landscape evolution of the Byrock region, NW NSW. *In:* Roach I.C. ed. *Advances in Regolith.* CRC LEME, pp. 144-148.

TAYLOR G. & EGGLETON R.A. 2001. *Regolith geology and geomorphology*. John Wiley & Sons, Chichester, 375 p.

WHITE D.E., HEM J.D. & WARING G.A. 1963. Chemical composition of subsurface waters. *In:* FLEISCHER M. ed. *Data of Geochemistry.* USGS Professional Paper 440-F.