RARE-EARTH ELEMENT GEOCHEMISTRY OF SELECTED SAMPLES FROM THE SULLIVAN Pb-Zn SEDEX DEPOSIT: THE ROLE OF ALLANITE IN MOBILIZING RARE-EARTH ELEMENTS IN THE CHLORITE-RICH FOOTWALL (82G/12)

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(Contribution No. 4, Sullivan-Aldridge project)

KEYWORDS: Economic geology, Sullivan mine, lithogeochemistry, rare-earth elements.

INTRODUCTION

This is a preliminary reconnaissance survey of rare-earth element (REE) geochemistry (supported by major and trace element geochemistry) of selected rock samples representing various alteration types at the sediment-hosted Sullivan lead-zinc sedex deposit, British Columbia.

We report the occurrence of very fine grained (<30μm) allanite (REE-rich epidote group mineral) in the chlorite-altered mineralized footwall, and in the albite-chlorite alteration zone at the Sullivan mine. The presence of allanite (Plate 2-5-1) identified in the mineralized, chlorite-altered footwall and the albite-chlorite altered hangingwall of the deposit is accompanied by an apparent increase in rare-earth element concentration in the footwall. The close textural relationship between chlorite, allanite, titanite, pyrrhotite, sphalerite and galena suggests that the crystallization of this assemblage was more or less contemporaneous. Thus, allanite formation was either contemporaneous with mineralization, or with post-ore alteration that was associated with some remobilization of the ore. The selective crystallization of the REE-rich epidote in the mineralized chlorite (±biotite) alteration zones implies one of two things: a rare-earth element gradient was superimposed on the rocks during alteration and mineralization, or less likely, the present rare-earth element concentration predated mineralization, and allanite may have formed after the light REE-rich phosphate, "metamorphic monazite", that reportedly occurs in the carbonaceous sediments of the Lower Aldridge Formation. In either case, as the abundance of allanite is accompanied by elevated rare-earth element values or significant rare-earth element fluctuation, combining detailed petrography with rare-earth element geochemistry could serve as a potential tool for identifying target areas that host mineralization. Allanite has been previously identified in the tourmalinitized footwall of the western part of the Sullivan ore zone by Campbell and Ethier (1984), in a biotite and garnet alteration zone within quartzite at North Star Hill by Delaney (1975), and in the granophyric part of the Purcell (Moyie) sills by Bishop (1974). Allanite grains in this study can be identified by their wide pleochroic halo which is the result of radiation damage to the host mineral by the decay of uranium (Plate 2-5-1). Because of the pleochroic halo around the grains, they may be mistaken for zircon.

Metamorphic monazite has been reported in the dark grey carbonaceous bands of siltite in the Aldridge Formation by Huebschman (1973). Fine-grained monazite was described as aggregates within the bands. The mode of occurrence of allanite in the chloritized and mineralized footwall in this study is significantly different: in the chloritized footwall, allanite overgrows or is intimately intergrown with pyrrhotite and galena, and the wide pleochroic halo around the grains suggests a high uranium content in the mineral (Plate 2-5-1).

ANALYTICAL TECHNIQUES

Rare-earth element geochemistry of selected rocks was determined by instrumental neutron activation analysis at the SLOWPOKE reactor at the University of Toronto. Sample preparation and analytical procedures followed the guidelines set out by Barnes and Gorton (1984). Major

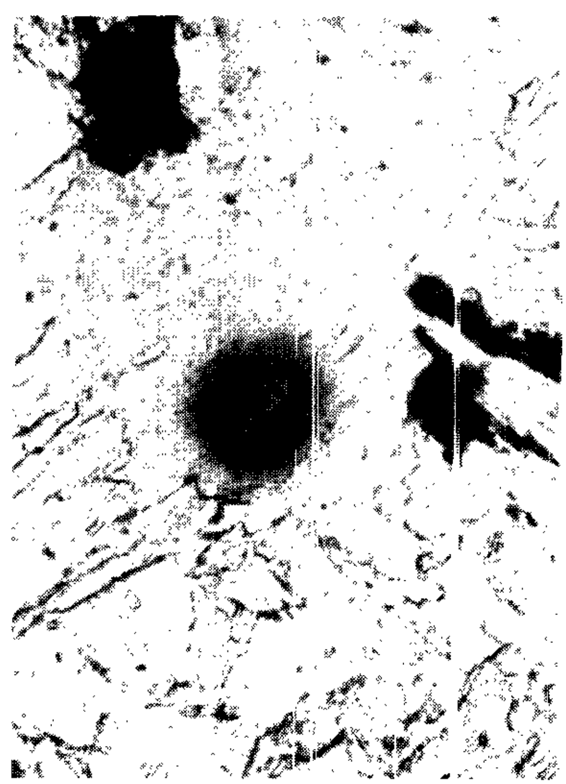

Plate 2-5-1. Allanite with pleochroic halo, in chlorite. Field: 2.3 mm. Plane polarized light.

TABLE 2-5-1
PETROGRAPHIC SUMMARY OF ANALYSED SAMPLES FROM AND AROUND THE SULLIVAN DEPOSIT

# and Loc.	Rock Type	Mineral Assemblage	Description
S-1 G-13-30	Pebble congl. (argillite)	qtz-carb-bio-ep-musc- gnt-po-sph-cp	Garnetized, fine-gr. siltstone
S-2 G-13-30	Moyie sill gabbro	amph-plag-ru-mag-ilm- ep-qtz-carb-po-cp	Epidote-amph. altered. coarse gr. gabbro
S-3 G-13-30	tourm. breccia	qtz-tourm-musc-bio-ru- mag-po	Fine-gr. siltstone repl. by tourmaline
S-4 P-10-4	chlorite rock crosscuts ore	chl-carb-gnt-po-mag-titan- all-zr	Chloritized, carbonatized siltstone
S-5 R-10-30	chlorite rock- footwall	chl-carb-po-gal-titan-all-ru sph-cp-boulangerite-zr	Med.-gr. chloritized, foliated titanite-rich siltstone/wacke
S-6 R-10-30	chlorite rock- footwall	chl-carb-titan-all-ru-bio- zr-qtz-apatite. scheelite	Med.-gr., foliated chloritized titanite-rich siltstone/wacke
S-8 N-10	'albitite'	ab-qtz-chl-py-mag-all-ru-zr	Med.-gr. albitized and chloritized siltstone/wacke
S-10 Moyie R.	Middle Aldridge Marker horizon	qtz-musc-carb-bio-mag-tourm	Very fine-gr. carbonaceous argillaceous siltstone
S-11 North Star Hill	Lower Aldridge siltstone	qtz-bio-chl-sphal-goeth-mag- gnt-all-zr	Very fine-gr. laminated argillaceous siltstone
S-14g Lumberton sill	Moyie sill gabbro	amph-plag-qtz-ep-mag- ilm.-ru-carb-bio-po-cp	Epidotized,amphibolitized coarse gr. gabbro
S-14p	'granophyre'	qtz-musc-ab-ep-chl-ru-mag-amph	sediment inclusion in gabbro

Underlining denotes dateable minerals. Abbreviations: ab:albite, all:allanite, amph:amphibole, bio: biotite, carb: carbonate, chl:chlorite, cp:chalcopyrite, ep:epidote, gal:galena, gnt:garnet, ilm:ilmenite, mag:magnetite, musc:muscovite, goeth=goethite, plag:plagioclase, po:pyrrhotite, py:pyrite, qtz:quartz, ru:rutile, sph:sphalerite, titan:titanite, tourm:tourmaline, zr:zircon.

TABLE 2-5-2
MAJOR, TRACE AND REE GEOCHEMISTRY OF SELECTED ROCKS FROM THE SULLIVAN MINE AND ITS AREA

#	S1	S2	S3	S4	S6	S8	S10	S11	S14g	S14p
SiO_2	61.7	51.4	66.1	30.5	26.2	59.8	68.1	65.9	50.5	62.0
TiO_2	0.20	1.15	0.55	0.63	0.80	0.72	0.65	0.58	0.72	0.44
Al_2O_3	5.22	13.0	11.3	15.0	17.8	17.8	16.5	13.0	14.6	13.8
Fe_2O_3*	3.68	13.4	12.7	20.4	20.2	4.67	3.25	7.30	10.3	5.75
MnO	1.00	0.32	0.02	1.08	0.72	0.07	0.04	0.16	0.15	0.09
MgO	1.63	6.01	1.76	17.4	18.4	2.68	1.20	1.34	8.36	3.99
CaO	13.4	8.52	0.21	2.45	0.60	0.68	0.19	0.06	10.0	7.88
Na_2O	0.06	1.34	0.72	0.02	0.03	9.24	1.01	0.07	1.59	3.09
K_2O	1.39	0.49	0.08	1.49	0.02	0.10	4.88	4.51	0.45	0.52
P_2O_5	0.09	0.11	0.11	0.11	0.08	0.09	0.13	0.08	0.07	0.06
LOI	9.54	2.31	2.93	8.23	10.05	2.70	2.62	6.23	2.70	1.77
TOTAL	98.0	98.1	96.6	97.4	95.4	98.7	98.8	99.4	99.5	99.5
(ppm)										
Cr	19	106	41	50	78	62	47	42	276	72
Co	6	37	21	2	0	3	7	13	37	22
Sc	3	44	8	10	16	16	13	10	38	20
Zr	174	91	328	343	362	338	266	350	50	243
Mo	0.50	0	1.40	1.10	1.40	1.50	0.30	1.80	0.20	0.20
Au	1.8	0.8	2.2	1.1	1.7	1.5	1.7	2.7	1.3	2.7
Rb	72	14	1	90	3	7	170	155	18	12
Ba	100	44	10	60	0	35	820	600	100	115
Th	4.40	1.90	10.90	11.40	17.70	15.40	13.00	11.00	1.50	7.30
U	1.10	0.33	2.90	3.20	4.50	4.10	3.60	3.00	0.10	1.30
La	23.00	8.10	22.40	10.20	67.70	17.90	36.20	62.40	5.60	19.70
Ce	51.80	20.60	50.40	21.90	147.10	45.30	76.40	143.60	11.00	46.10
Nd	20.90	9.40	20.80	10.00	57.70	24.10	27.00	53.00	5.40	19.70
Sm	5.15	3.22	5.00	2.80	12.80	9.00	6.30	11.90	1.84	5.47
Eu	0.82	1.08	1.12	0.99	3.85	1.30	0.84	2.48	0.55	0.99
Tb	0.94	0.83	0.83	0.48	1.68	1.30	0.87	1.10	0.36	1.00
Yb	3.00	2.30	3.50	2.50	6.86	4.65	3.94	4.10	1.55	3.45
Lu	0.44	0.39	0.54	0.44	1.00	0.74	0.60	0.62	0.24	0.58

* Total Fe expressed as Fe_2O_3, g=gabbro, p=sediment clot in gabbro.

element analysis was obtained on fused disks by x-ray fluorescence (X-Ray Assay Laboratory, Toronto). The rocks analyzed were collected during a visit to the mine in the fall of 1990. Samples were selected from alteration types that would most likely contain dateable hydrothermal accessory minerals such as rutile and titanite (Hamilton *et al.*, 1982; Leitch, 1991). Detailed petrographic study preceded analysis in order to determine the mineralogy and the textural relationships between alteration assemblages. Allanite was identified by electron microprobe. A summary of mineralogy, texture and the sample locations is given in Table 2-5-1, whole-rock geochemistry in Table 2-5-2 and microprobe analysis of selected allanite grains in Table 2-5-3.

REE GEOCHEMISTRY OF ALTERED ROCKS

Various rock types were selected for analysis in order to identify alteration type(s) associated with REE mobility and subsequently with the abundance of allanite. The samples included gabbro from the Moyie sills in the mine, pebble conglomerate in the footwall of the laminated ore, tourmalinized breccia, albitized sediment and chloritized sediment from the footwall. In addition, gabbro with a 'granophyric' inclusion was collected from the Lumberton sill at Moyie Lake, south of Cranbrook as well as Lower Aldridge siltstone from North Star Hill immediately south of the deposit, and siltstone from the lower Middle Aldridge marker unit (Hiawatha marker). The rare-earth element composition of the analyzed rocks is discussed below.

The two samples of Moyie sill gabbro have a flat rare-earth element pattern typical of rocks of tholeiitic basalt composition and it is in agreement with the tholeiitic basalt composition determined by trace and major element chemistry for most Moyie sills in southern British Columbia (Höy, 1989; Figure 2-5-1). However, there is a distinct chemical difference between the gabbro from the mine (S-2) and the gabbro from the Moyie Lake area (S-14g, Table 2-5-2); the former has higher rare-earth element concentration, it is higher in scandium and lower in chromium, rubidium and barium, which indicates that it is either a more fractionated equivalent of the gabbro from Moyie Lake, or that the two are unrelated. The comparable lanthanum:ytter-

TABLE 2-5-3
MICROPROBE ANALYSES* OF MINERALS FROM THE SULLIVAN MINE†

	ALLANITE		APATITE
SiO_2	32.16	31.19	0.0
Al_2O_3	17.53	17.92	0.0
CaO	10.80	9.61	54.61
FeO	13.94	14.72	0.46
P_2O_5	0.0	0.0	42.47
La_2O_3	5.09	4.58	0.0
Ce_2O_3	12.35	11.36	0.0
Nd_2O_3	3.54	4.32	0.0
SO_3	0.56	0.0	0.0
TOTAL	95.97	94.72	97.55

* Semiquantitative analyses due to the overlap of some REE peaks
† Analyses are from S-6 (chlorite footwall)

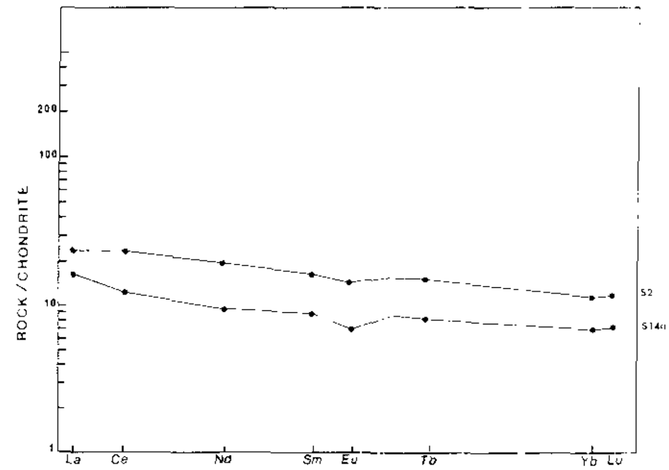

Figure 2-5-1. Rare-earth element pattern of gabbros from the Moyie sills.

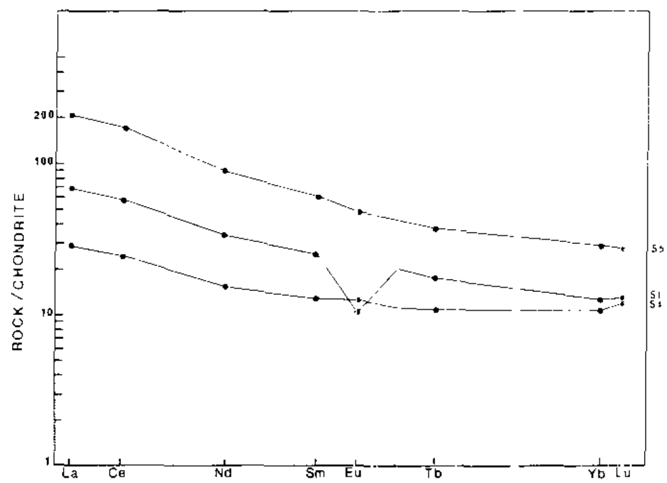

Figure 2-5-2. Rare-earth element pattern of pebble conglomerate (S1), chloritized footwall (S6) and chloritized rock in a fault (S4).

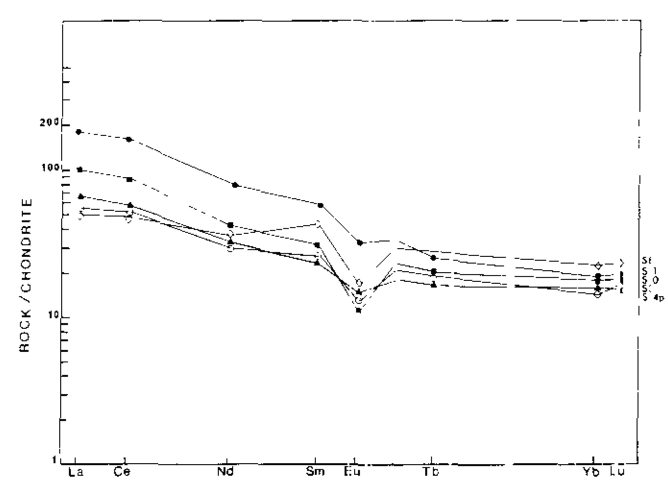

Figure 2-5-3. Rare-earth element pattern of altered sediments.

Plate 2-5-2a. Sediment inclusion ('granophyre') in the Lumberton sill gabbro. Both fields 5.8 mm. Crossed polars.

Plate 2-5-3. Allanite grains in chlorite-rich albitite. Field: 0.8 mm. Plane polarized light.

Plate 2-5-2b. Gabbro from the Lumberton sill.

Plate 2-5-4. Allanite and pyrrhotite in chlorite. Field: 0.8 mm. Plane polarized light.

bium ratios suggest that the rare-earth element abundances have not been disturbed in these rocks during extensive epidotization, and that the difference in their concentration is a primary feature. The 'granophyre' pod or inclusion (S-14p), 0.5 by 0.5 metre in size, in the Lumberton sill represents a fragment of fine-grained sediment (Plate 2-5-2a). Textural evidence and rare-earth element concentrations (Table 2-5-2) suggest a sedimentary precursor to this inclusion in the gabbro (Plate 2-5-2b). The low REE concentration in the gabbros, coupled with the absence of allanite, suggest that rare-earth mobility was insignificant within the gabbros during their emplacement and during subsequent hydrothermal alteration.

The sediments in the mine have been overprinted by various types of alteration, including tourmaline, chlorite, albite, garnet and pyrite (Hamilton *et al.*, 1982; Leitch and Turner, 1991; Leitch *et al.*, 1991). Although the mineralogy of some sediments may be distinctly different, the similarity in REE concentrations implies that the REE were 'fixed' in the rocks prior to alteration and were not disturbed subsequently. For example, S-1 (pebble conglomerate), S-3 (tourmalinized breccia), S-8 (albitized sediment with only minor chlorite) and S-14p (sediment fragment in gabbro) all display comparable rare-earth element trends (negative europium anomaly) and concentrations (Figures 2-5-2 and 3), but their mineralogy is significantly different (Table 2-5-1). This suggests that tourmalinitization, albitization, garnetization and epidotization of the rocks were not accompanied by significant mobilization of rare earths. It should be noted here that in the albitized sample, S-8, REE concentrations are not particularly high, and allanite grains are sparse, whereas in samples in which albite is accompanied by extensive chlorite alteration, the number of allanite grains increases five to tenfold (Plate 2-5-3).

The major element concentration in S4 and S6 basically reflects the extensive chlorite alteration observed in the rocks, thus the original nature of the rock is difficult to infer (Table 2-5-1). Looking at the elements least likely to have been disturbed by chloritization (Zr, Th), S4 and S6 are distinct in having unusually high zirconium and thorium concentrations. Furthermore, the zirconium and thorium concentrations in these samples cover the range of similarly high concentrations in the Aldridge sediments (Table 2-5-1). Thus we infer that S4 and S6 are chloritized sediments. S4 and S6 have significantly different rare-earth concentrations. However, as there is evidence for significant rare-earth mobility in the chlorite alteration zones, localized concentration and depletion associated with the chlorite alteration is expected.

The chlorite-rich sample (S-6) which was collected from the mineralized footwall of the orebody is distinguished by its elevated rare-earth concentration (Figure 2-5-2) and its lack of a negative europium anomaly. The high REE values are accompanied by the presence of allanite in the chlorite (Plates 2-5-4 and 5). The close textural association of chlorite, allanite, titanite and pyrrhotite (Plates 2-5-6, 7 and 8) and galena (Plate 2-5-9) in the mineralized rock suggests that the crystallization of these phases was more or less contemporaneous. Although it should be noted that while pyrrhotite is often overgrown by allanite, galena is often intergrown with the allanite grains.

Based on relative REE concentrations, Richards (1989) reported some correlation in concentrations of individual stratigraphic horizons in the Pritchard Formation (USA) and those in the Aldridge Formation, suggesting that the Sullivan horizon is also recognizable in the Belt Basin. He concluded that the similarity between Pritchard and Aldridge tourmalinite rare-earth concentration indicated a similar origin and that rare-earth elements could be used for stratigraphic correlation. Our work indicates significant rare-earth variation between tourmalinized and chlorite-altered rocks and hence we maintain that alteration type is the main variable that influences rare-earth mobilization in Sullivan mine rocks.

A siltstone with comparably high rare-earth concentration (S-11, Figure 2-5-3) was collected from the upper part of altered Lower Aldridge Formation on North Star Hill. This fine-grained rock is characterized by a high pyrrhotite content and biotite alteration. Allanite grains generally occur either in the biotite, or are intergrown with pyrrhotite.

DISCUSSION AND CONCLUSIONS

This preliminary study is a precursor to a comprehensive geochemical investigation of REE concentration and mobility associated with alteration and mineralization in various rock types at the Sullivan deposit and the surrounding area, and an investigation concerning the role of the Moyie sills in mineralization (Hamilton *et al.*, 1982; Hoy, 1989).

The significance of the presence of allanite in the chlorite-altered mineralized footwall, and in the albite-chlorite alteration zone at the mine is twofold by recognizing a high REE gradient (accompanied by allanite concentration) or significant REE fluctuation, we may define a possible zone of mineralization, distinguishing it from the 'barren' alteration zones; and possible dating of allanite by U-Pb geochronology may define the age of mineralization. The reported occurrence of allanite in the granophyric zones of the Purcell (Moyie) sills (Bishop, 1974) is not surprising, as rare earths are common constituents (often as monazite) of some carbonaceous sediments. Therefore, the melting or partial melting of included sediments in the gabbro, and the contemporaneous (?) crystallization of allanite with the emplacement and subsequent deuteric alteration (epidotization of feldspars) of the sills suggests the scavenging of rare earths from remelted sediments. The crystallization of allanite under such specific conditions does not negate the importance of its association with mineralization. More significant is the allanite vein reported by Campbell and Either (1984), who recognized large (300 µm) allanite grains crosscutting tourmalinized Aldridge sediments. This is in agreement with our observations with respect to the hydrothermal origin of the minerals around the ore. Because REE tend to favor precipitation under reducing conditions (Schandl and Gorton, 1991), we would expect a REE gradient (enrichment and/or fluctuation) around sulphide orebodies. Rare-earth element enrichment around several Archean massive sulphide deposits has been reported by Campbell *et al.* (1984) and Schandl and Gorton (1991), and a current study funded by the Ontario Geological Survey Research Grant Program is under way to investigate the impact of this rare-earth element halo on exploration

Plate 2-5-5. Allanite and pyrrhotite in chlorite. Field: 0.8 mm. Plane polarized light.

Plate 2-5-7. Allanite rims pyrrhotite. Field: 0.8 mm. Plane polarized light.

Plate 2-5-6. Titanite (large centre grain) and small allanite grains (with pleochroic halos) in chlorite. Field: 0.8 mm. Plane polarized light.

Plate 2-5-8. Allanite intergrown with pyrrhotite in chlorite. Field: 0.8 mm. Plane polarized light.

Plate 2-5-9. Allanite intergrown with galena, in chlorite. Field: 0.8 mm. Plane polarized light.

(Schandl *et al.*, 1991). In this preliminary study, the textural relationship between allanite, sphalerite, galena and chlorite suggests that mineralization was contemporaneous with the mobilization of rare-earth elements and with the crystallization of allanite in the localities studied. The source of rare-earth elements may have been the "metamorphic monazite" (Heubschman, 1973) or other rare-earth element-rich minerals in the carbon-rich horizons of the Lower and Middle Aldridge. Work is in progress for detailed rare-earth element studies of the Moyie sills and the altered zones in the Lower and Middle Aldridge sediments, and the U-Pb geochronology of hydrothermal alteration around the Sullivan orebody.

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