

# Corkite from Aggeneys, Bushmanland, South Africa

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## Abstract

Corkite associated with plumbojarosite and goethite occurs in gossan and iron-formation at Black Mountain and Broken Hill, Aggeneys. Electron microprobe analyses indicate that there are two groups of corkite present in the area; one with high Cu and low  $(\text{PO}_4)^{3-}$  and the other with low Cu and high  $(\text{PO}_4)^{3-}$  contents. This can be explained in terms of the general formula  $AB_2(XO_4)_2(\text{OH})_6$ , where the incorporation of divalent ions in the B site is accompanied by the exchange of trivalent anions by divalent ones to retain charge balance. Complete solid-solution is inferred between  $(\text{SO}_4)^{2-}$  and  $(\text{PO}_4)^{3-}$  end members, indicating that the jarosite and beudantite groups form part of the same solid-solution series. The distribution of Zn in corkite also reflects the regional distribution of zinc grades in the area, becoming more zinc-rich from west to east. New X-ray diffraction parameters are also presented which update existing data.

**KEYWORDS:** corkite, EMP analyses, solid-solution series, X-ray diffraction data, Bushmanland, South Africa.

## Introduction

THE Proterozoic rocks of which Bushmanland is composed consist of a great diversity of types and include gneisses, metavolcanics and metasediments. Iron-formation (BIF) of the Algoma-type occurs in these Proterozoic metasediments as isolated units many of which are frequently associated with base metal mineralization in the upper part of the Gams Member of the Hotson Formation (Colliston *et al.*, 1989). These iron-formation (BIF), associated ferriferous metasediments (magnetite quartzites) and gossans contain a wide variety of secondary minerals formed by weathering and oxidation of disseminated pyrite, pyrrhotite, chalcopyrite, galena and sphalerite. Species of secondary minerals are especially numerous at Black Mountain, Broken Hill and the Aggeneys mountains (Fig. 1). For example the occurrence of creaseyite at Black Mountain is the first on the African continent (Meyer *et al.*, 1986), but other sulphate-phosphate minerals are also present (Table 1).

## Mineralogy

Numerous secondary minerals were found in the gossan and iron-formations (Table 1). In Bushmanland, corkite, a rare pale yellow to greenish mineral of the beudantite group, was

identified during a recent study (Meyer, 1986) at Broken Hill and also at the Black Mountain gossan, where it occurs in very small quantities in cavities, associated with plumbojarosite and goethite.

As a result of the sparse (micro gram) quantities of corkite available, material was removed from thin sections and hence the small sample X-ray diffraction technique (Hiemstra, 1956) was applied to aid with the identification of this mineral (Table 2). The unit cell parameters of corkite were refined using the least-squares method of Appleman *et al.* (1972) and the results were compared to those described for corkite in the literature (Table 3). From these data it is evident that the material from Black Mountain corresponds well with corkite from literature (Table 3).

## Chemistry

Corkite was analysed with a Cameca Camebax electron microprobe using a 15 kV accelerating voltage, a 20 nA beam current and a 2  $\mu\text{m}$  beam diameter. Mineral standards and ZAF correction techniques were utilized. The data are presented in Table 4.

When considering the composition of the corkite samples from the Aggeneys area, there is a

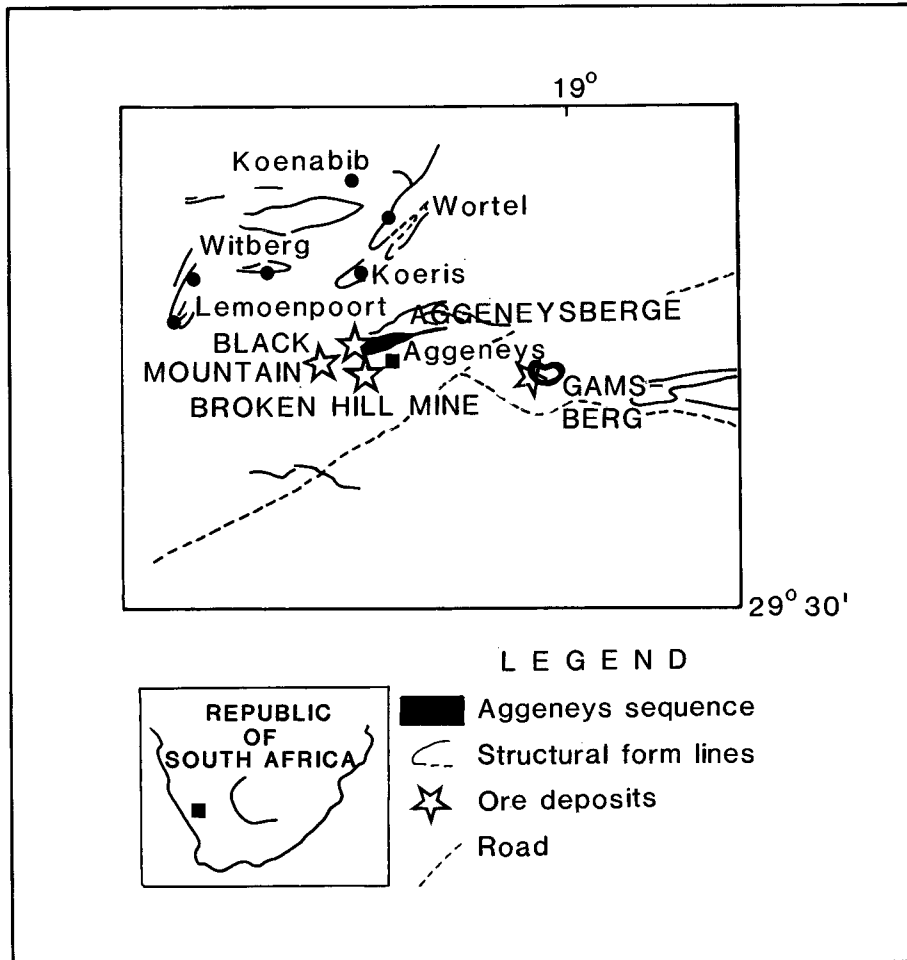


Fig. 1. Locality map depicting the distribution of ore deposits at Black Mountain, Broken Hill, Aggeneys Mountains and Gamsberg.

TABLE 1: Secondary minerals occurring in the iron-formation and gossan at Aggeneys and environs, Bushmanland.

SILICATES	SULPHATES	PHOSPHO-SULPHATES	PHOSPHATES
creaseyite* chrysocolla diopside	plumbojarosite linarite alunite kalinite brochantite gypsum	corkite	dufrenite* turquoise
CARBONATES-SULPHATES	CARBONATES	CHLORIDES	
caledonite leadhillite	cerussite calcite	atacamite diaboleite	

\* Indicates mineral data previously published by the authors.

TABLE 2: X-Ray diffraction data for corkite from Black Mountain, Aggeneys, Bushmanland.

$l/l_0$	d calc	d obs	h	k	l	$l/l_0$	d calc	d obs	h	k	l
75	5.869	5.87	1	0	1	5	1.979	1.99	0	1	8
10	5.580	5.55	0	0	3	30	1.956	1.96	3	0	3
10	5.011	5.01	0	1	2	10	1.932	1.94	1	2	5
30	3.619	3.60	1	1	0	20	1.810	1.82	2	2	0
5	3.472	3.46	1	0	4	5	1.736	1.75	2	0	8
100	3.033	3.03	1	1	3	5	1.680	1.68	2	1	7
40	2.945	2.94	0	1	5	5	1.670	1.67	3	0	6
15	2.780	2.79	0	0	6	5	1.612	1.63	1	0	10
30	2.506	2.50	0	2	4	10	1.542	1.55	3	1	5
10	2.346	2.35	2	1	1	10	1.540	1.54	0	4	2
10	2.284	2.28	2	0	5	10	1.474	1.48	0	1	11
			1	2	2	5	1.433	1.44	3	2	1
30	2.228	2.24	1	0	7	5	1.405	1.41	1	3	7
5	2.204	2.21	1	1	6	5	1.390	1.39	0	0	12
5	2.060	2.06	2	1	4	5	1.360	1.36	3	2	4

114.6 mm Debye-Scherrer camera, Cu  $K_{\alpha}$  radiation, Ni filter  
(Cu  $K_{\alpha}$  = 1.5418 Å)

Unit cell parameters:  
System = Hexagonal  $a_0$  = 7.239 (0.005) Å  
Spacegroup = R3m  $c_0$  = 16.681 (0.013) Å  
 $V$  = 757.068 (0.943) Å<sup>3</sup>

TABLE 3: Unit cell parameters for corkite, beaverite and lusungite.

	1	2	3	4	5	6	7	8	9	10
$a_0$	7.239	7.276	7.278	7.280	7.22	7.26	7.203	7.20	7.234	7.04
$c_0$	16.681	16.849	16.813	16.821	16.66	16.77	17.19	16.94	17.14	16.80
Vol	757.068	772.439	771.00	772.05	752.11	765.49	772.384	760.52	776.78	721.08

1. Corkite from Black Mountain, South Africa.
2. Corkite from Black Mountain, South Africa (Cu-rich variety).
3. Corkite from De Richelle, Belgium (Fransolet *et al.*, 1977).
4. Corkite from Dernbach, Hessen-Nassau, Germany (Giuseppetti and Tadini, 1987).
5. Corkite from the Glendore mine, Cork, Ireland (Nambu *et al.*, 1964).
6. Corkite from Kivu, Congo (Van Wambeke, 1971).
7. Beaverite from the Osarizawa mine, Japan (Taguchi *et al.*, 1972).
8. Beaverite from Utah, U.S.A. (Taguchi *et al.*, 1972).
9. Beaverite from Caribou, New Brunswick (Jambor and Dutrizac, 1983).
10. Lusungite from Kobokobo, Kivu, Congo (PDF 14-58).

general lack of K in their structures. As inferred from the work of Scott (1987), this is typical of BIF-hosted samples. These samples, with the exception of one, all fall in the beudantite group of the jarosite supergroup (Scott, 1987). Sample number 5, however, plots in the lusungite group (Table 4, Fig. 2).

When the chemical analyses are recalculated to formula contents according to the system described by Scott (1987) where  $(XO_4) = 2$  and  $B = 3$  (Table 4), all samples with the exception of one (number 2, Table 4) show a depleted  $B$  site occupancy. This again corresponds to the findings of Scott (1987). Because of Fe contamination, sample 2 was compensated to a value of 0.02 mol  $Fe^{3+}$  to agree to the  $B = 3$  mol rule.

Corkite from the Aggeneys area can be divided

into two groups, viz. one low in CuO and high in  $P_2O_5$  (1–6, Table 4), and the other high in CuO and low in  $P_2O_5$  (7–11, Table 4). The sulphate content of the first group is also considerably lower than that of the second, which can be attributed to the substitution of  $(SO_4)^{2-}$  by  $(PO_4)^{3-}$ . Samples 5 and 6 from Broken Hill are enriched in zinc relative to that in samples from Black Mountain; this result is in accord with the trend of higher zinc grades from west to east within the Aggeneys area. Corkites from the Glendore Mine and Dernbach (Nambu *et al.*, 1964) (12 and 13, Table 4) fall somewhere between groups 1 and 2 as defined above. The Pb content of sample 12, however, is considerably lower than that of the other corkite samples.

A plot of  $(A^{2+} + A^{3+})$  (mol) against  $(XO_4)^{3-}$

TABLE 4: Chemical composition and structural formulae of corkite from Aggeneyns and corkite and beaverite from literature.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Al <sub>2</sub> O <sub>3</sub>	0.12	2.58	0.02	0.44	0.71	0.95	0.07	0.08	0.05	0.06	0.06	-	-	4.69	3.64	3.51
Fe <sub>2</sub> O <sub>3</sub>	33.14	32.35	32.30	33.77	29.82	31.67	29.63	31.92	29.14	28.04	29.42	40.69	34.61	16.43	17.28	17.99
P <sub>2</sub> O <sub>5</sub>	11.63	12.92	16.18	13.96	18.11	11.66	7.89	8.86	8.17	8.63	7.95	8.97	9.35	-	-	-
SO <sub>3</sub>	12.67	10.16	7.52	9.15	6.47	11.81	15.78	14.80	15.92	15.18	15.44	13.76	12.72	23.32	21.32	22.92
SiO <sub>2</sub>	-	-	-	-	-	-	-	-	-	-	-	-	-	1.58	-	-
As <sub>2</sub> O <sub>5</sub>	-	-	-	-	-	-	-	-	-	-	-	0.24	-	-	-	-
PbO	33.03	32.54	32.46	32.38	33.63	32.66	32.65	32.31	32.49	33.30	33.02	24.05	32.33	32.40	29.44	29.87
CuO	0.03	0.60	2.19	0.51	1.20	0.17	5.19	3.60	4.85	5.01	4.82	2.45	1.35	11.09	9.70	11.69
ZnO	0.27	0.24	0.10	0.49	1.70	2.33	0.00	0.06	0.12	0.00	0.01	-	-	0.15	-	-
H <sub>2</sub> O*	4.79	7.83	6.23	7.13	5.48	7.32	7.32	7.58	6.94	6.64	7.25	9.77	8.45	8.70	9.02	8.12
H <sub>2</sub> O	-	-	-	-	-	-	-	-	-	-	-	-	-	0.56	-	0.17
Insol.	-	-	-	-	-	-	-	-	-	-	-	-	0.56	-	10.05	5.92
TOTAL	97.68	99.22	97.00	97.83	97.12	98.57	98.53	99.21	97.68	96.86	97.97	99.93	99.37	98.92	100.45	100.19

\* calculated for samples 1 - 11 using scheme of Scott (1987)

Structural formulae:

- |   |       |  |
|---|-------|--|
| 1 - Pb <sub>0.92</sub> (Fe <sub>2.58</sub> Al <sub>0.02</sub> Zn <sub>0.02</sub> Cu <sub>0.01</sub> ) <sub>2.63</sub> (PO <sub>4</sub> ) <sub>1.02</sub> (SO <sub>4</sub> ) <sub>0.98</sub> (OH) <sub>4.68</sub>  | 1-4   | corkite from Black Mountain, Aggeneyns (present study)             |
| 2 - Pb <sub>0.94</sub> (Fe <sub>2.60</sub> Al <sub>0.33</sub> Cu <sub>0.05</sub> Zn <sub>0.02</sub> ) <sub>3.00</sub> (PO <sub>4</sub> ) <sub>1.18</sub> (SO <sub>4</sub> ) <sub>0.82</sub> (OH) <sub>5.63</sub>  | 7-11  |  |
| 3 - Pb <sub>0.90</sub> (Fe <sub>2.51</sub> Cu <sub>0.17</sub> Zn <sub>0.01</sub> Al <sub>0.00</sub> ) <sub>2.69</sub> (PO <sub>4</sub> ) <sub>1.42</sub> (SO <sub>4</sub> ) <sub>0.58</sub> (OH) <sub>4.30</sub>  | 5-6   | corkite from Broken Hill, Aggeneyns (present study)                |
| 4 - Pb <sub>0.93</sub> (Fe <sub>2.72</sub> Cu <sub>0.04</sub> Zn <sub>0.04</sub> Al <sub>0.01</sub> ) <sub>2.51</sub> (PO <sub>4</sub> ) <sub>1.26</sub> (SO <sub>4</sub> ) <sub>0.74</sub> (OH) <sub>5.09</sub>  | 12    | corkite from the Glendore mine, Cork, Ireland (Nambu et al., 1964) |
| 5 - Pb <sub>0.90</sub> (Fe <sub>2.22</sub> Zn <sub>0.12</sub> Cu <sub>0.09</sub> Al <sub>0.08</sub> ) <sub>2.51</sub> (PO <sub>4</sub> ) <sub>1.52</sub> (SO <sub>4</sub> ) <sub>0.48</sub> (OH) <sub>3.62</sub>  | 13    | corkite from Dembach, Hessen-Nassau, Germany (Nambu et al., 1964)  |
| 6 - Pb <sub>0.94</sub> (Fe <sub>2.54</sub> Zn <sub>0.18</sub> Al <sub>0.12</sub> Cu <sub>0.02</sub> ) <sub>2.86</sub> (PO <sub>4</sub> ) <sub>1.05</sub> (SO <sub>4</sub> ) <sub>0.95</sub> (OH) <sub>5.21</sub>  | 14    | beaverite from the Osarizawa mine, Japan (Taguchi et al., 1972)    |
| 7 - Pb <sub>0.95</sub> (Fe <sub>2.41</sub> Cu <sub>0.42</sub> Al <sub>0.01</sub> Zn <sub>0.00</sub> ) <sub>2.84</sub> (SO <sub>4</sub> ) <sub>1.28</sub> (PO <sub>4</sub> ) <sub>0.72</sub> (OH) <sub>5.27</sub>  | 15-16 | beaverite from Utah, U.S.A. (Taguchi et al., 1972)                 |
| 8 - Pb <sub>0.93</sub> (Fe <sub>2.59</sub> Cu <sub>0.29</sub> Al <sub>0.01</sub> Zn <sub>0.01</sub> ) <sub>2.89</sub> (PO <sub>4</sub> ) <sub>1.19</sub> (PO <sub>4</sub> ) <sub>0.81</sub> (OH) <sub>5.43</sub>  |       |  |
| 9 - Pb <sub>0.93</sub> (Fe <sub>2.32</sub> Cu <sub>0.39</sub> Al <sub>0.01</sub> Zn <sub>0.01</sub> ) <sub>2.73</sub> (SO <sub>4</sub> ) <sub>1.27</sub> (PO <sub>4</sub> ) <sub>0.73</sub> (OH) <sub>4.91</sub>  |       |  |
| 10 - Pb <sub>0.96</sub> (Fe <sub>2.26</sub> Cu <sub>0.41</sub> Al <sub>0.01</sub> Zn <sub>0.00</sub> ) <sub>2.68</sub> (SO <sub>4</sub> ) <sub>1.22</sub> (PO <sub>4</sub> ) <sub>0.78</sub> (OH) <sub>4.74</sub> |       |  |
| 11 - Pb <sub>0.97</sub> (Fe <sub>2.42</sub> Cu <sub>0.40</sub> Al <sub>0.01</sub> Zn <sub>0.00</sub> ) <sub>2.83</sub> (SO <sub>4</sub> ) <sub>1.27</sub> (PO <sub>4</sub> ) <sub>0.73</sub> (OH) <sub>5.28</sub> |       |  |
| 12 - Pb <sub>0.72</sub> (Fe <sub>2.79</sub> Cu <sub>0.21</sub> ) <sub>3.00</sub> (SO <sub>4</sub> ) <sub>1.14</sub> (PO <sub>4</sub> ) <sub>0.84</sub> (AsO <sub>4</sub> ) <sub>0.02</sub> (OH) <sub>5.37</sub>   |       |  |
| 13 - Pb <sub>1.00</sub> (Fe <sub>2.88</sub> Cu <sub>0.12</sub> ) <sub>3.00</sub> (SO <sub>4</sub> ) <sub>1.09</sub> (PO <sub>4</sub> ) <sub>0.91</sub> (OH) <sub>5.97</sub>                                       |       |  |
| 14 - Pb <sub>1.00</sub> (Fe <sub>1.41</sub> Al <sub>0.63</sub> Si <sub>0.18</sub> Cu <sub>0.09</sub> Zn <sub>0.01</sub> ) <sub>2.32</sub> (SO <sub>4</sub> ) <sub>2.00</sub> (OH) <sub>5.04</sub>                 |       |  |
| 15 - Pb <sub>0.99</sub> (Fe <sub>1.54</sub> Cu <sub>0.92</sub> Al <sub>0.54</sub> ) <sub>3.00</sub> (SO <sub>4</sub> ) <sub>2.00</sub> (OH) <sub>6.03</sub>   |       |  |
| 16 - Pb <sub>0.93</sub> (Fe <sub>1.49</sub> Cu <sub>1.03</sub> Al <sub>0.48</sub> ) <sub>3.00</sub> (SO <sub>4</sub> ) <sub>2.00</sub> (OH) <sub>5.85</sub>   |       |  |

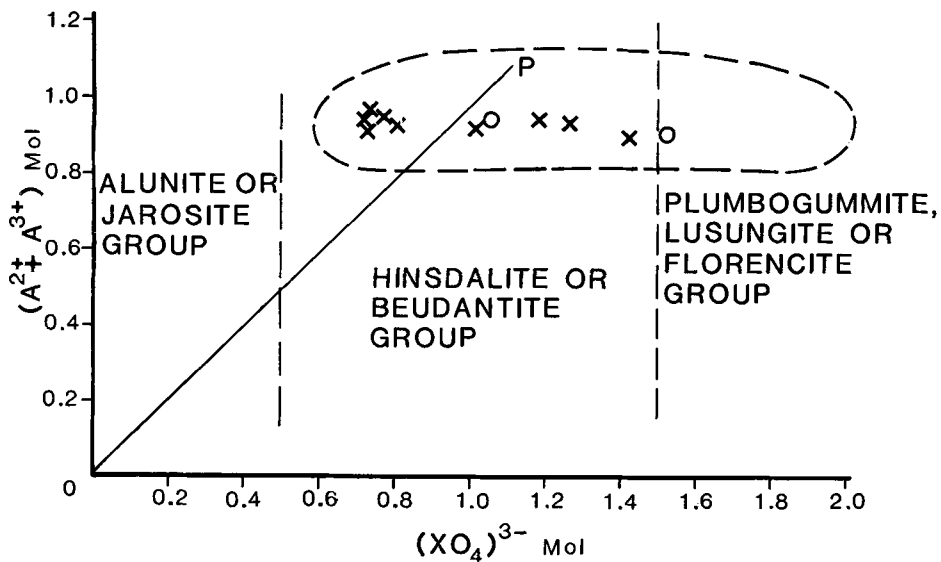


Fig. 2. Plot of divalent and trivalent cations in A sites relative to trivalent anions in  $XO_4$  sites in samples from Aggeneyns. Compositional fields, the perfect substitution line (O-P) and the field of BIF-hosted samples after Scott (1987).

shows that all the samples from the Aggeneys area falls in the field defined for BIF-hosted samples (Scott, 1987) (Fig. 2). Five of the samples from Aggeneys (samples 7–11, Table 4), however, plot considerably ( $>0.1$  mol) above the 1:1 substitution line as defined by Scott (1987). It is significant that these samples all contain an appreciable amount of Cu while  $(\text{SO}_4)^{2-}$  exceeds  $(\text{PO}_4)^{3-}$ , thus falling in the second group as defined above.

In a plot of  $A^{2+}$  (mol) against  $\text{Fe}^{3+}$  in  $B$  sites (mol) (Fig. 3), it appears that the samples from Aggeneys fall along the zone defined for the BIF-associated samples, implying that the  $A$  sites are more than 80% filled. The average  $A$  site occupancy is 94% for the samples from the second group above. The substitution as defined by Scott (1987) whereby electrostatic neutrality is maintained by a combination of vacancies in the  $A$  sites and Cu and Zn substitution in  $B$  sites is superimposed on the substitution of  $[A^{2+} + (\text{XO}_4)^{3-}]$  for  $[A^+ + (\text{XO}_4)^{2-}]$ , is not entirely valid in the case of the Aggeneys samples. In this instance the  $A$  site remains bivalent and the charge balance is retained by substitution in both the  $B$  ( $\text{Fe}^{3+}$  by  $\text{Cu}^{2+}$ ) as well as the  $\text{XO}_4$  sites.

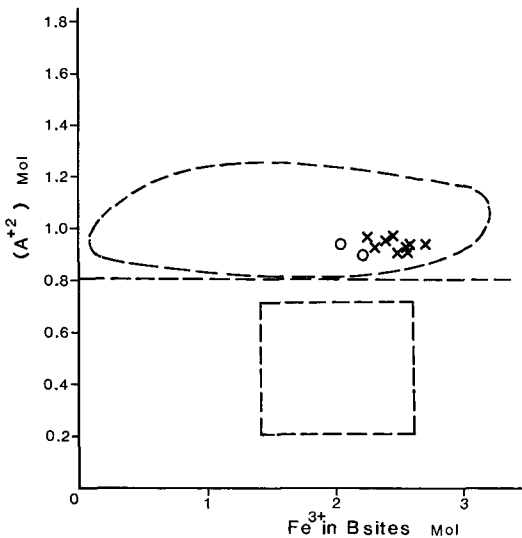


Fig. 3. Plot of divalent cations in  $A$  sites relative to the  $\text{Fe}^{3+}$  concentration of the  $B$  sites in the samples from Aggeneys. The immiscibility field represented by square on figure, zone of complete solid solution and the field of BIF-associated samples after Scott (1987).

When the data from Aggeneys are plotted on a diagram depicting the  $(\text{XO}_4)^{3-}$  (mol) versus

$\text{Fe}^{3+}$  in  $B$  sites (mol), then it is evident that only a number of the samples correspond to the field where complete solid solution is evident, i.e.  $(\text{XO}_4)^{3-} > 1.1$  mol (Scott, 1987) (Fig. 4). Some samples, however, fall below the 1.1 mol line and some even fall within the immiscibility field of the Queensland samples.

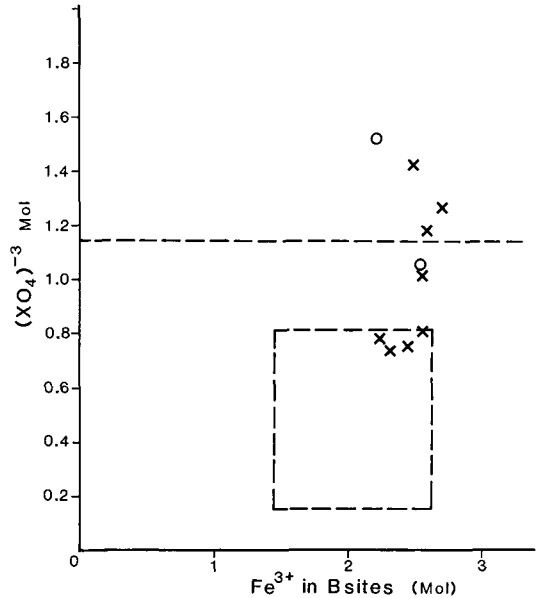


Fig. 4. Plot of trivalent anions in  $\text{XO}_4$  sites relative to  $\text{Fe}^{3+}$  in  $B$  sites for samples from Aggeneys. The zone of immiscibility represented by square on figure and the area of complete solid solution after Scott (1987).

When all the data from Aggeneys and Australia (Scott, 1987) are considered with regard to the replacement of  $(\text{SO}_4)^{2-}$  by  $(\text{PO}_4)^{3-}$  and the substitution of  $\text{Al}^{3+}$  by  $\text{Fe}^{3+}$ , then it is clear that linear relationships ( $r=0.9999$  and  $r=0.9906$ ) exists. It can therefore be deduced that a complete solid-solution series exists between the sulphate and phosphate end members on the one hand as well as the aluminium and ferric end members on the other hand.

### Conclusions

Jambor and Dutrizac (1983) concluded that substitution of  $\text{Fe}^{3+}$  by  $\text{Cu}^{2+}$  is sufficient to form a compositional series from plumbojarosite to beaverite. Subsequently Jambor and Dutrizac (1985) synthesized the plumbojarosite–beaverite solid-solution series.

Although it was thus far not possible to bridge the gap between the jarosite (or alunite) and the beudantite (or hinsdalite) groups as defined by Scott (1987), the data presented here corroborate the findings of Scott (1987) that there is complete solid-solution series between the different subgroups. On the basis of complete substitution of  $(\text{SO}_4)^{2-}$  by  $(\text{PO}_4)^{3-}$ , this even extends into the lusungite (plumbogummite and florencite) group of the alunite and jarosite supergroups. Because of Al and Fe substitution which attains a regression coefficient of 0.99, there is solid solution even between the alunite and jarosite supergroups.

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### References

- Appleman, D. E., Evans H. T., and Handwerker D. S. (1972) Geol. Surv. Computer Contribution, 20, Geol. and Comp. Centre Divisions, Washington, DC, Program no. W9214, 26 pp.
- Colliston, W. P., Praekelt, H. E., and Schoch, A. E. (1989) A broad perspective (Haramoep) of geological relations established by sequence mapping in the Proterozoic Aggeneyns terrane, Bushmanland, South Africa. *S. Afr. J. Geol.* **92**, 42–8.
- Fransolet, A. M., Jedwab, J., and Van Tassel R. (1977) Mineraux secondaires plombifères (cerusite, angle-site, pyromorphite, corkite et wulfenite) de Richelle, Belgique. *Ann. Soc. Geol. Belg.* **100**, 1–7.
- Giuseppetti, G. and Tadini, C. (1987) Corkite,  $\text{PbFe}_3(\text{SO}_4)(\text{PO}_4)(\text{OH})_6$ , its crystal structure and ordered arrangement of the tetrahedral cations. *Neues Jahrb. Mineral. Mh.*, 71–81.
- Hiemstra, S. A. (1956) An easy method to obtain X-ray diffraction patterns of small amounts of material. *Am. Mineral.* **41**, 519–21.
- Jambor, J. L. and Dutrizac, J. E. (1983) Beaverite-plumbojarosite solid solutions. *Can. Mineral.* **21**, 101–13.
- (1985) The synthesis of beaverite. *Ibid.* **23** 47–51.
- Meyer, T. Q. (1986) *The mineralogy and geochemistry of some of the iron-formations of Bushmanland*. Unpubl. M.Sc. thesis, Univ. Orange Free State, Bloemfontein, South Africa, 193 pp.
- Van der Westhuizen, W. A., Beukes, G. J., De Bruijn, H., and Schoch, A. E. (1986) An occurrence of the hydrous lead-copper-iron silicate creaseyite in South Africa. *Mineral. Mag.* **50**, 346–8.
- Nambu, M., Tanida, K. and Kano, S. (1964) Corkite from the Osarizawa Mine, Akita Prefecture. *Japan Assoc. Mineral. Petrol. Econ. Geol.* **52**, 113–21.
- Scott, K. M. (1987) Solid solution in, and classification of, gossan-derived members of the alunite-jarosite family, northwest Australia. *Am. Mineral.* **72**, 178–87.
- Taguchi, Y., Kizawa, Y. and Okada, N. (1972) On beaverite from the Osarizawa Mine. *Kobutsugaki Zasshi (Japan)*, **10**, 313–25.
- Van Wambeke, L. (1971) Hinsdalite and corkite: indicator minerals in Central Africa. *Mineral. Deposita*, **6**, 130–2.

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