Electron-microprobe analysis of anandite

PATTIARATCHI, Saari, and Sahama (1967) have described a new barium-rich brittle mica (anandite) from the magnetite ore zone of the Wilagedera iron ore body, in the North-western Province of Ceylon. They concluded that the chemical composition of anandite corresponds to the simplified formula $(Ba,K)(Fe,Mg)_3(Si,Al,Fe)_3O_{10}(O,OH)_2$ after correcting their analyses for probable admixed pyrite contamination (cf. table I).

A sample of this interesting mica was made available to us by D. B. Pattiaratchi through A. R. Crawford of this Department and a preliminary analysis with an electron microprobe indicated certain important points at variance with previously published analyses of this mineral: lower Al_2O_3, TiO_2, and K_2O and higher total iron and MnO values. Of even greater interest was the conclusion that the S content believed by Pattiaratchi *et al.* (1967) to be a result of pyrite contamination is in fact a primary constituent of the mineral anandite. The importance of these conclusions led to a more intensive study of the mineral using the electron microprobe combined with a new partial chemical analysis carried out on specially purified and hand-picked mineral grains.

A polished thin section containing a number of anandite grains was prepared thin enough for the grains to be transparent and observed to be free of inclusions of pyrite or any other contaminating phases. These grains were then analysed on the ARL electron microprobe in this Department using a number of well-analysed silicate minerals as standard materials. The analyses of a number of grains showed no significant variation in composition between grains and the mean composition is given in table I. These new data indicate that the Al_2O_3, TiO_2, and K_2O contents previously reported seem to be too high while the previous total iron values appear to be low. It has also been established that the relatively high sulphur content found is a primary constituent in the anandite structure and is not due to sulphide contamination. The electron microprobe data also indicate that anandite contains a significant chlorine content in the lattice.

A partial chemical analysis was then carried out by E. Kiss of this Department using methods described previously (Kiss, 1967 and unpublished work) on a specially purified concentrate of anandite grains that had also been hand-picked to remove a considerable number of contaminating phases. The results of this partial analysis (table I) confirm the electron microprobe values for Al_2O_3, TiO_2, K_2O, MnO, and total iron and appear to generally confirm the previous determinations of the Fe^{2+}/Fe^{3+} ratio in anandite. However, during the determination of Fe^{2+} it was observed that H_2S was evolved during the dissolution of the mineral with a hydrofluoric/sulphuric acid mixture (Kiss, 1967) and it is very likely that some Fe^{3+} was reduced at this time. There is, then, good reason for believing that the Fe^{2+}/Fe^{3+} ratio reported in table I is too high.

TABLE I. Comparison of chemical analyses of anandite

	1	2	3	4	4 *a*		
SiO_2	25·22	25·20	n.d.	25·04	Si	5·13	8·00
Al_2O_3	5·86	4·85	0·67	0·67±0·08	Al	0·16	
TiO_2	0·32	0·28	0·03	0·05±0·02	Ti	0·00	
Fe_2O_3	6·47	6·98	5·48	—	Fe^{2+}	2·71	
FeO	33·42	33·10	36·61*	—			
MnO	0·70	0·66	0·94	1·21±0·03	Fe^{3+}	4·47	5·58
MgO	3·18	3·39	n.d.	2·95	Mg	0·90	
BaO	19·60	20·35	21·86	20·84	Mn	0·21	
CaO	0·15	0·16	n.d.	$<$ 0·07			
Na_2O	0·15	0·10	0·21	0·20±0·04	Ba	1·67	1·84
K_2O	0·95	0·93	0·31	0·36±0·08	Na	0·08	
H_2O^+	2·01	1·98	n.d.	n.d.	K	0·09	
H_2O^-	0·12	0·12	n.d.	n.d.			
S	2·52	2·96	n.d.	3·05	S	1·17	1·39
Cl	n.d.	n.d.	n.d.	0·63	Cl	0·22	
	100·67	101·06	—	—			
O ≡ S,Cl	1·26	1·48	—	—			
Total	99·41	99·58	—	—			
Total iron as FeO	39·35	39·49	41·66	42·04			

n.d. not determined.

* Probably too high. Evolution of H_2S during HF/H_2SO_4 dissolution of anandite for Fe^{2+} determination may have reduced some Fe^{3+}.

1. Analysis by J. P. R. Fonseka and N. R. de Silva uncorrected for supposed pyrite contamination (Pattiaratchi *et al.*, 1967).
2. Analysis by O. von Knorring uncorrected for supposed pyrite contamination (Pattiaratchi *et al.*, 1967).
3. Partial wet chemical analysis by E. Kiss (this work).
4. Electron microprobe analysis (this work).

4 *a*. Structural formula calculated on water-free basis relative to 22 oxygen atoms.

Electron microprobe analyses were made on the contaminating mineral phases separated from the anandite grains during the preparation of the purified sample used for chemical analysis. It was found that the anandite grains contained considerable amounts of included minerals including sulphides, zircon, apatite, fluorite, and calcite, the major contaminating phases being an augite and a titanium-rich biotite with analyses given in table II. From these data it is clear that the discrepancies between the previous analyses and the present work could be explained in a qualitative manner if the original analyses were carried out on material containing some biotite and augite contamination.

TABLE II. Electron microprobe analyses of major silicate inclusions in anandite crystals

	1	2	1 *a*			2 *a*		
SiO_2	51·98	35·48	Si	1·99	2·00	Si	5·42	8·00
Al_2O_3	0·13	12·97	Al	0·01		Al	2·34	
TiO_2	0·53	5·09				Ti	0·24	
FeO*	13·04	21·68	Ti	0·01	2·00	Ti	0·35	5·77
MnO	1·88	0·32	Fe	0·42		Fe	2·76	
MgO	11·72	11·50	Mg	0·67		Mg	2·62	
			Mn	0·06		Mn	0·04	
CaO	20·01	$< 0·07$	Ca	0·82				
Na_2O	0·35	0·31	Na	0·02		K	1·98	2·07
K_2O	$< 0·03$	8·45				Na	0·09	
Total	99·64	97·49†						

* Total iron reported as FeO.
† Water and fluorine contents not determined.

1. Augite.
1 *a*. Augite structural formula based on 6 oxygen atoms.
2. Biotite.
2 *a*. Biotite structural formula calculated on water-free basis relative to 22 oxygen atoms.

Since it was not possible to determine the (OH) content of anandite in the present work, the structural formula based on the electron microprobe analyses and given in table I has been calculated on the basis of 22 oxygen atoms. In the absence of an accurate Fe^{2+}/Fe^{3+} ratio determination the amount of Fe^{3+} present has been assumed to be sufficient to fill the *Z* group tetrahedral sites. It now appears that the new brittle mica anandite contains a relatively large content of S and smaller amount of Cl in the lattice. The question then arises whether the S content is present as SO_4^{2-} or S^{2-} ions.

A separate study has been made (Lovering and Widdowson, 1968) on the electron microprobe of the wavelength shift of the S-Kα radiation as a function of the presence of SO_4^{2-} or S^{2-} ions in mineral lattices. The results of this study have shown that the wavelength of the S-$K\alpha$ peak from anandite is characteristic of S^{2-} ions. This result is also consistent with the observation that H_2S was evolved during the acid dissolution of the mineral as described previously. The similarity in ionic radius between S^{2-} (1·84 Å) and Cl^- (1·81 Å) suggests that both ions replace OH^- (1·40 Å) ions in the anandite structure.

Acknowledgements. The authors wish to thank Mr. H. Berry and Mr. R. Rudowski for their careful preparation of a purified anandite sample; Mr. E. Kiss for his partial chemical analysis; Dr. I. A. Threadgold of the Department of Geology, University of Sydney, for general discussion on the sulphur bonding problem.

Department of Geophysics and Geochemistry,
Australian National University,
Canberra, A.C.T., Australia.

J. F. Lovering
J. R. Widdowson

References

Kiss (E.), 1967. Anal. Chim. Acta, vol. 39, p. 223.
Lovering (J. F.) and White (A. J. R.), 1964. Journ. Petrology, vol. 5, p. 195.
—— and Widdowson (J. R.), 1968. Lithos, vol. 1.
Pattiaratchi (D. B.), Saari (E.), and Sahama (Th. G.), 1967. Min. Mag., vol. 36, p. 1.

[*Manuscript received 30 January 1968*]

Kaersutite from the minverite of Cornwall

The Devonian spilitic suite in Cornwall includes sills of proterobase, albite diabase, and picrite (Dewey and Flett, 1911). The proterobase of St. Minver was named minverite by Dewey (1910) and consists of purplish titan-augite, fresh dark brown hornblende, and traces of olivine, together with biotite, albite, ilmenite, and apatite, more or less altered to chlorite, saussurite, epidote, leucoxene, and other secondary minerals. The dark brown hornblende has usually been referred to as barkevikite (by Dewey and others) but in a personal communication to the writer (1960) M. E. Cosgrove regarded it as kaersutite. Lehmann (1963) places it in the kaersutite–syntagmatite series (in the sense of Tröger, 1956, p. 76) and gives the following optical properties: α, 1·673–5; β, 1·693–6; γ, 1·703–5; $2V_\alpha$, 76° to 82°; γ: [001], 6° to 16°. In the absence, to the writer's knowledge, of an analysis, a sample was separated from a British Museum specimen (B.M. 1920/583 (3)) and an analysis made by A. J. Easton. This is given in the table below,