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A NEW ANALYSIS OF COSSYRITE FROM THE ISLAND OF PANTELLERIA

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Evidence is accumulating that convinces the crystallographer that the mineral called cossyrite should be assigned to aenigmatite. Unfortunately, the convention used in presenting the results as unit cell content does not permit one to compare them readily with the all important corresponding chemical analyses. It is also possible that it may conceal the results of a poor analysis.

Kelsey and McKie (1964) in their excellent paper have calculated the unit cell contents of seventeen aenigmatites (including cossyrite). It is obvious, when one scans the corresponding chemical analyses,¹ together with those of Bussen and Dudkin (1962), that the cell can take care of diverse ingredients, present in widely varying concentrations, without difficulty.

The analyses referred to also include a sample of cossyrite collected by Soellner (1909) on Pantelleria and analyzed for him by Dittrich, who was the first to show that TiO_2 was an essential constituent and that his sample contained 1.29 per cent H_2O^+ also as an essential constituent. This amount can be easily fitted into the unit cell. The writer, however, strongly steeped in chemical lore, feels that if such an amount of H_2O is an essential constituent we must admit that cossyrite differs from aenigmatite.

Carmichael (1962), in his paper on the pantelleritic liquids, records two new analyses of samples of cossyrite isolated directly from museum specimens of obsidian pantellerites collected in Pantelleria. Unlike Dittrich, he found very little H_2O . Did Dittrich, an excellent analyst, err in making his analysis, or did he analyze an impure sample? Soellner found on the rim of Cuddia di Mida, a volcano on the island of Pantelleria, an assemblage of free crystals in which cossyrite had been concentrated. He selected with the aid of a hand lens what he considered the best crystals.

Urged on by a desire to find a solution to what seemed to be discordant results and by a desire to see the island of Pantelleria, whose rocks and minerals have aroused a great deal of interest, the writer visited the

¹ A summary of aenigmatite and cossyrite analyses was presented by Fleischer (1936). Kelsey and McKie (1964) give references to the analyses of the seventeen aenigmatites discussed in their paper.

island in March of 1963, accompanied by Dr. G. Vianelli of the Istituto di Mineralogia dell'Universita di Palermo. Thanks to the many courtesies extended to us by Comm. Rag. Vincenzo Almanzo, the Sindaco of Pantelleria, we reached the rim of the volcano Cuddia di Mida where Soellner made his collections. Unfortunately, we could not locate the black and white patches described by him because a scrubby vegetation now covered much of the area; at a somewhat lower elevation, however, we found such patches. Some thirty pounds of the melange¹ of altered pumice, black crystals mixed with quartz, feldspar, and glass were gathered and shipped to Palermo, where a small sample of the dried mixture was treated with bromoform, enabling us to isolate the black crystals. When these were very finely ground and examined under the microscope we noted an appreciable concentration of cinnamon colored cossyrite and green pyroxene. Some of the difficulties that would be encountered in isolating clean cossyrite became obvious in this preliminary work. Many of the crystals of cossyrite had coatings of what seemed to be opaline silica; many others were coated with an oxide of iron. Many of the larger grains were contaminated with inclusions of pyroxene and adhering volcanic glass. In spite of all this, it was obvious that the material we had collected contained a high percentage of cossyrite, probably as much as 5 per cent, but it was also obvious that great care would have to be taken in order to obtain a pure sample.

The crude concentrate was shipped to the Geophysical Laboratory where the coarse stones and organic trash were sifted out and the balance was "washed" onto a vibrating Wilfley table. The black heavy concentrate was dried at 105° C. Some of the largest black crystals were hand picked, the stubby ones (presumably cossyrite) separated from the slender (pyroxene) prisms. Very finely ground cossyrite has a cinnamon red color whereas the associated pyroxene is grayish green, but in spite of this difference in color the unaided eye is of little use in distinguishing pure cossyrite from pyroxene. The impurities referred to above were identified under the microscope. Microscopic examination indicated, however, that if the mixture of crystals (cossyrite and pyroxene) were reduced in size a good separation of cossyrite from extraneous material could be obtained. Therefore, the heavies from the Wilfley table were crushed by impact and the portion sized between 150 and 200 mesh was thoroughly deslimed. A ceramic hand magnet was used to remove strongly magnetic particles. The balance, approximately 300 grams, was passed through a Frantz magnetic separator as modified by Faul and

¹ This material occurs in an area where rivulets, by a kind of riffing effect, have brought about a concentration of heavy black minerals.

Davis (1959). By careful control, it proved possible to further concentrate the heavies until they contained about 60 per cent of dull looking cossyrite.

The sample was now divided into lots of about 10 grams each and each lot was treated with dilute hydrofluoric acid (1:10) at room temperature. This operation removed the opal-like coating without attacking the cossyrite. The HF was thoroughly washed out with H₂O. The shiny black crystals were washed into a heavy walled rubber finger cot, kneaded for about 5 minutes, washed by decantation, and the slimes rejected. The attrition produced by the kneading loosened the iron oxide and removed most of the attached glass.

The clean, dried (105° C.) crystals were divided into lots that could be easily handled in a medium sized separatory funnel. A Clerici solution was used to remove olivine and, on dilution, to separate cossyrite from pyroxene and the residues of feldspar and quartz. By what can best be described as a kind of asymptotic procedure, a density was found that gave the best separation of clean cossyrite from cossyrite with glass still attached. Those who have had experience in using a Clerici solution will recognize that this is the most difficult part of the operation, for the change in density of the solution caused by changes in air temperature can be troublesome. Material ground finer than 200 mesh was not used because it was not thoroughly "wetted" by the Clerici solution. The various portions of clean cossyrite were filtered, thoroughly washed first with warm water, finally with pure acetone, and dried at 105° C. The complete operation is tedious but it enables one to obtain a generous amount of very clean cossyrite. F. Chayes performed the final operation, a count of the very small number of particles that retained some attached glass or locked grains of pyroxene.¹ G. L. Davis examined the cossyrite for the presence of thallium by the very sensitive method of α -ray spectrometry. None was found. Obviously, the Clerici solution had been thoroughly removed.

Kelsey and McKie, with considerable justification, infer that in years gone by the difficulty of obtaining clean aenigmatite was greater than the difficulties experienced in making an analysis free from analytical error.

¹ The final concentrate for analysis was split into size fractions 120-150, 150-200, and a carefully deslimed sand which passed the 200 mesh sieve. Three microsamples were drawn from each of these fractions and submitted to grain counting, in the process of which nearly 12,000 grains were counted. The results for the different microsamples were very similar, with an overall average of less than 0.1 per cent each of pyroxene and olivine. An incomplete selvage of glass was noted on about 4 per cent of the cossyrite grains, but as this almost certainly comprises less than 10 per cent by volume of any grain on which it is found it cannot amount to more than a few tenths per cent of the specimen as a whole.

This is probably true, but even now if one is compelled to work with material such as we were obliged to use in order to check on the Soellner-Dittrich results one must use very great care in isolating a sample pure enough for chemical analysis. It just does not make sense to subject impure material to detailed chemical analysis and subsequent ratiocination.

There are a number of pitfalls that must be avoided when analyzing such a complex mineral as aenigmatite (cosyrite). The ease with which titanium hydrolyzes can be quite troublesome. Then too, there is a real difficulty involved in accurately determining the small amounts of alumina that are usually present. The method of obtaining a value by difference after all the other oxides in the R_2O_3 group have been evaluated is not a sound one. The procedure of determining it in the filtrate¹ obtained from the precipitate of titanium by cupferon, leads to somewhat more satisfactory results. Physical methods such as are employed when using either the x-ray spectrometer or the electron probe may soon help in obtaining more accurate analyses of all of the constituents than can be obtained now, but it is, of course, essential that an empirical background derived from wet analysis must first be obtained. At present, the large ferrous iron content of aenigmatite and cosyrite must be determined by wet procedures, which fortunately can be very accurately done by the modified Pratt method.

In addition to the bulk analysis, two density determinations were made with the aid of a pycnometer. Ample material was available for using samples weighing approximately 4 grams. The usual precautions of eliminating air were observed. The two values are 3.817 and 3.813, both at 22° C.

The results shown in column 3 of the table of analyses (Table 1) represent an average obtained when the various constituents were analyzed by different procedures. The question concerning the H_2O content is answered; the clean cosyrite obtained from the assemblage of crystals similar to the one described by Soellner contains little or no water. Dittrich describes the Penfield method used by him in determining the H_2O content. There is no doubt in my mind that his value is correct. The same method was used in obtaining my own very low result. The analyses by Carmichael and Zies are in good agreement. Cosyrite contains little or no water.

It is difficult to account for Dittrich's value of 1.29 per cent. It is quite possible that he had impure material to work with. Soellner selected his material with the help of a hand lens, which precluded his being able to recognize pyroxene and glass inclusions in the dense black crystals. He

¹ The organic matter must, of course, be first destroyed.

also had difficulty in obtaining good signals from the faces of his cossyrite. This could have been due to the presence of the opal-like coating previously mentioned. Dittrich found more Fe_2O_3 than Zies, and much more than Carmichael; it is quite possible that his crystals were contaminated by an oxide or iron. When we allow for these differences the analysis of Dittrich is similar to those of Carmichael and Zies.

TABLE 1. ANALYSES OF COSSYRITE FROM THE ISLAND OF PANTELLERIA

	Carmichael ¹		Zies ²	Dittrich ³	Gossner and Spielberger ⁴
	2A	3A			
SiO_2	41.02	40.97	40.93	4.83	42.47
TiO_2	8.92	8.83	8.71	8.21	7.95
Al_2O_3	0.94	0.89	0.24	0.20	1.11
Fe_2O_3	1.31	1.19	2.60	5.31	1.59
FeO	38.84	38.86	38.45	34.72	38.31
MnO	1.16	1.08	1.15	1.39	1.74
MgO	0.07	0.54	0.49	0.57	0.50
CaO	0.45	0.55	0.55	0.77	2.49
Na_2O	7.36	6.93	6.93	6.61	3.66
K_2O	0.06	0.08	0.04	trace	
H_2O^+	—	nil	0.02	1.29	
H_2O^-	—	0.07	nil		
Cl		n.d.	⁵		
F		n.d.	n.d.		
	100.13	99.99	100.11	99.90	99.82

¹ Carmichael, 1962, p. 96.² Zies, this presentation.³ Dittrich, average of two analyses given in Soellner, 1909, p. 539.⁴ Gossner and Spielberger, 1930, p. 135.⁵ None found.

The very low Na_2O and high CaO found by Gossner and Spielberger (1930) suggest that their sample contained a "sodic ferrohedenbergite" of the type isolated and analyzed by Carmichael (1962, p. 91). The ferric iron content recorded by Gossner and Spielberger, however, is incompatible with this suggestion.

The author has retained the name cossyrite to designate the mineral found on Pantelleria. The amounts of what may be called extraneous constituents are smaller in cossyrite than those shown in any of the analyses of aenigmatite. In this respect they approach more nearly the idealized formula suggested by Kelsey and McKie, namely



More *x*-ray and phase studies will be required to obtain a better understanding of aenigmatite, a term that covers a wide variation in chemical composition. Such studies may show that new, accurate chemical analyses of very carefully selected samples are demanded. Perhaps when the remaining enigmatical characteristics of aenigmatite are cleared up the name aenigmatite will no longer be applicable.

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Michael Fleischer called my attention to the work of Bussen and Dudkin in which are recorded three new analyses of aenigmatites; they are illustrative of the wide range in their composition. I am also indebted to him for a stimulating discussion of the chemical aspects of the aenigmatite problem. I am deeply indebted to F. Chayes for critically reviewing the manuscript.

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EFFECTS OF MAGNESIUM ON THE FORMATION OF APATITE

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INTRODUCTION

Apatite, approximately $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ or the fluorine analog, is widely distributed in nature. It occurs as hard parts of organisms and in igneous, metamorphic, and sedimentary rocks. Magnesium likewise is common in