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COULSONITE, FeV2O4, A SPINEL-TYPE MINERAL FROM LOVELOCK, NEVADA

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Abstract

Coulsonite, FeV_2O_4 or $FeO \cdot V_2O_3$, previously named and recognized from India, but only vaguely described, has been identified in magnetite-bearing rocks from the Buena Vista Hills east of Lovelock, Nevada. In polished section the mineral is bluish-gray in color with its powder varying between dark brown to black. H=4.5 to 5. Coulsonite shows a mean reflectivity of 23.5 determined with a slit microphotometer using green light. Under crossed nicols coulsonite appears isotropic although occasionally it is weakly anisotropic. The mineral is isometric, space group Fd3m, with a=8.297 Å, and 8 formula units per unit cell. G(meas.)=5.17 to 5.20, and G(calc.)=5.15.

Occurrence

Coulsonite, $FeO \cdot V_2O_3$, is found closely associated with magnetite and chlorine-rich scapolite in the metamorphosed igneous rocks of the Buena Vista Hills located some twenty miles southeast of the town of Lovelock in western Nevada. The host rock is hornblende andesite and the evenly distributed fine-grained magnetite probably represents a primary constituent in the rock.

Veinlets of magnetite, in association with chlorine-rich scapolite, apatite, sphene, and alkali pyroxenes and amphiboles, cut the andesite. They represent metasomatic activity with the introduction of chlorine, fluorine, phosphorus, sodium, and potassium, and a considerable amount of iron (Radtke, 1963). Coulsonite is only found with these late magnetite veinlets, reflecting an addition of vanadium along with the elements listed above.

Coulsonite occurs along the octahedral planes in magnetite and less commonly as subhedral crystals isolated in a matrix of scapolite, chlorite, hornblende and muscovite. The first type may have been formed by exsolution of vanadium from magnetite followed by limited replacement of magnetite by coulsonite localized at octahedral plane intersections (Figs. 1 and 2). The second type of coulsonite, spatially separated from magnetite, was used in the study and is shown in Figs. 3 and 4.

INTRODUCTION

Vanadium-rich magnetite was first reported by Heron (1936) in reference to "vanado-magnetite" ores from India. The occurrence of vanadium in titaniferous iron ores was discussed by Dunn and Dey (1937). They suggested that the mineral previously named "coulsonite" by Dunn (1937), in honor of Dr. A. L. Coulson of the Indian Geological



FIG. 1. (lower left) Exsolution texture of coulsonite (light gray) along octahedral planes of magnetite (dark gray). Silicate gangue minerals are present in minor amounts (black). Note coulsonite replacing magnetite between grain boundaries as shown at tip of arrow from right edge of plate. $225 \times .$

FIG. 2. (upper left) Oriented exsolution coulsonite (light gray) in magnetic (dark gray). Note sphene crystals locked within the magnetite as shown at tip of arrow from top margin of plate. $225 \times$.

FIG. 3. (lower right) Evenly disseminated fine-grained coulsonite in subhedral crystals (light gray) scattered through silicate gangue (dark gray), composed of chlorite, muscovite and scapolite. $135 \times$.

FIG. 4. (upper right) Veinlet of coulsonite (black), shown at tip of arrow, cutting altered hornblende andeste. Hornblende and sphene are shown in the upper right hand corner in contact with coulsonite. The light gray background is sericite and plagioclase altered to scapolite. Tiny apatite crystals are scattered throughout the rock. $80 \times .$

Survey, might be a vanadium maghemite. Additional support to this was given by Frankel and Grainger (1941), and the existence of a natural vanadium maghemite was accepted by Ramdohr and Schneiderhöhn (1931).

The close association between coulsonite and magnetite was emphasized by English (1939) by referring to coulsonite as a vanadiferous iron ore found as patches in magnetite. Palache *et al.*, (1944), mention coulsonite as a vanadiun magnetite found in gabbro rock at Bihar, India.

Chemical analyses of coulsonite available in the literature show the highest vanadium content previously reported to be 8.80 per cent V_2O_3 , (Dunn and Dey, 1937). This ore sample also contained 11.68 per cent TiO₂. Subtraction of the ilmenite from the analysis still does not make the vanadium content exceed that of the iron. For this reason most reference books refer to coulsonite as vanadium magnetite. The writer feels the reason for the difference between this chemical analysis and those given in Table 2 of this paper may be explained by the fact that coulsonite in the Indian ores only occurs along octahedral planes and in patches in magnetite making separation of the two for analysis impossible.

Synthetic FeV₂O₄ was studied by Ball *et al.*, (1954), and it was found that magnetite entered into solid solution with the vanadites at 1,000° C. They also concluded that synthetic FeV₂O₄ with additional ferrous oxide and heating showed no change in the size of the unit cell (a=8.45 Å). Addition of ferric oxide at a temperature of 1,000° C. caused a linear expansion of the unit cell varying from 2.9 to 6.1 per cent. Earlier work by Trömel and Gedschold (1948) showed that ferrous oxide enters the spinel phase at elevated temperatures.

Wyckoff (1951) shows V₂FeO₄ to have a=8.468 Å and Strunz (1957) determined the synthetic compound FeV₂O₄ to have a=8.49 Å. This discrepancy in unit cell size between that determined by the writer for natural spinel coulsonite and synthetic FeV₂O₄ is difficult to explain but could be partially accounted for by the presence of ferric oxide (Fe³⁺) in the artificial compounds.

The writer wishes to emphasize that this paragenesis is quite different from those described in the past for vanadium. The vast majority of titaniferous magnetites the world over are associated with gabbro and anorthosite. These ores contain vanadium as a minor constituent varying between 0.5 to 1.0 per cent. Rankama (1950) gives the average vanadium content in these ores as < 0.2 per cent. He also points out the vanadium magnetite (coulsonite) may contain up to 5 per cent vanadium in the oxide ores of iron. In the Buena Vista iron ores the only titanium present is in sphene and the host rock is hornblende andesite. The writer feels the Buena Vista ores are hydrothermal in origin somewhat removed from the

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magmatic origin usually described for magnetite ilmenite ores associated with basic rocks.

Description

Coulsonite is bluish-gray in color, but in powdered form it is dark brown to black. The mineral has a metallic luster and is isotropic under crossed nicols. Locally it is slightly anisotropic, resembling magnetite in this property.

In thin section coulsonite is opaque and must be distinguished from magnetite in reflected light. The mean reflectivity of coulsonite measured by a slit microphotometer in air using green light is 23.5. This value is slightly higher than that for magnetite determined under similar conditions at 21.4 in these specimens. Hematite present in certain samples has a mean reflectivity of 28.1 and is easily distinguished from the other opaque oxides. There is no visible internal reflection from coulsonite.

The hardness of coulsonite is estimated to be 4.5-5, and it is slightly softer than magnetite. The specific gravity, as determined from five samples, is 5.17-5.20. This compares closely with the calculated specific gravity of 5.15.

Coulsonite gives a negative reaction to all of the common microchemical etch tests (Dunn and Dey, 1937; Short, 1940). Aqua regia and hydrochloric acid applied to the mineral show no reaction. Since both of these reagents react with magnetite, their use provides a good method for distinguishing between these two associated minerals.

CHEMICAL ANALYSIS

The common association of magnetite and coulsonite necessitated extensive microscopic examination to locate samples containing coulsonite and lacking magnetite. These were crushed and the coulsonite was separated magnetically from the other minerals. The coulsonite concentrate was analyzed chemically as follows:

The ground sample was treated with a solution of one volume of concentrated sulfuric acid in four volumes of water at room temperature in an Erlenmeyer flask. The acid solution turned greenish-blue in color in approximately four minutes which deepened during the following seven days. The acid solution was agitated periodically throughout a 21 day period. The solution was then analyzed volumetrically following the method described by Furman (1925) and others.

This method necessitated some arbitrary decision in the calculation of the analyses. In this study all the vanadium was calculated as V_2O_3 , with the remaining reducing power as FeO, and the final iron as Fe₂O₃. The other alternative would have been to calculate all the iron as FeO, the remaining reducing power as V_2O_3 , and the final vanadium as V_2O_5 . The analyses show the presence of only a small amount of Fe and V in a higher valence state.

The results of the chemical analyses giving the chemical composition

and mole ratios of iron and vanadium are shown in Table 2. Samples 1 and 2 represent relatively pure coulsonite whereas sample 3 represents a concentrate composed of only 83.81 per cent by weight of acid soluble coulsonite. The remainder of this sample was composed of various silicate minerals, including sphene and hornblende, insoluble in (1+4) H₂SO₄ at room temperature.

The mole ratios given in Table 2 indicate the formula for the mineral is $FeO \cdot V_2O_3$. The mole ratios of analysis sample 3 depart only slightly from those of the other two analyses. This is true even though roughly 20 per cent of the sample was composed of other minerals. The higher content of ferric iron may reflect either a small amount of another iron oxide mineral in the sample or the partial replacement of V^{3+} by Fe^{3+} in the coulsonite structure.

CRYSTAL CHEMISTRY

Coulsonite is a mineral of the spinel group with a general structural formula AB_2O_4 . The first symbol (A) represents Fe^{2+} and the second symbol (B) includes V^{3+} and minor amounts of Fe^{3+} . This is expressed by the formula $Fe^{2+}(V, Fe)_2^{3+}O_4$ and for practical purposes may be written $Fe^{2+}V_2^{3+}O_4$.

TABLE 1. X-RAY POWDER DATA FOR COULSONITE

Calculated spacings based on isometric unit cell, space group Fd3m, a=8,297 Å. CrK α radiation (2.2909 Å), 114.7 mm, diameter camera. B indicates lines due to

I	d (meas.)	hk1	d (calc.) 4.789	
35	4.79	111		
58	2.93	022	2.934	
7	2.50	113	2.502	
100	2.50	113	2.502	
4	2.39	222	2.395	
78	2.07	004	2.075	
3	1.903	331	1.904	
28	1.693	224	1.694	
91	1.597	115	1.597	
		333		
95	1.466	044	1.467	
5	1.404	135	1.403	
10	1.312	026	1.312	
25	1.266	335	1.266	
18	1.249	226	1.251	
7	1.198	444	1.198	
3	1.162	117	1.162	
		155		

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	Sample 1		Sample 2		Sample 3	
	а	b	a	b	а	\mathbf{b}
		с		с		с
FeO	30.75	,428	27.92	.389	26.34	.367
		1.00		1,00		1.00
Fe ₂ O ₈	.52	.003	. 24	.002	2.01	,013
		0.01		0.01		0.04
V ₂ O ₃	68,41	.456	72.04	.481	55.46	.370
		1.07		1.24		1.01
Total	99.68		100.20		83.81	

TABLE 2. CHEMICAL ANALYSES OF COULSONITE

(a) Weight per cent analysis.

(b) Moles calculated.

(c) Mole ratios calculated with reference to FeO.

The mineral has a normal spinel structure corresponding to such compounds as $ZnFe_2O_4$ (Azaroff, 1960). The unit cell contains 8 formula units with 32 oxygen atoms arranged in a cubic closest packing. The metal atoms (A) are distributed in four-fold coordination among the tetrahedral voids and the (B) atoms in six-fold coordination among the octahedral voids. There is a partial substitution of Fe³⁺ for V³⁺ in the structure.

X-ray analysis shows that the mineral is isometric with $a=8.297 \pm 0.002$ Å, and the space group Fd3m. The calculated spacings based on the unit cell data and the observed intensities and spacings from a film made using Cr radiation are listed in Table 1.

The main criteria for the identification of coulsonite are its characteristic x-ray powder diffraction pattern and chemical composition. The unit cell dimensions and symmetry do not restrict the theoretical chemical composition, yet the chemical analyses in Table 2 show this to be a relatively pure natural end compound.

The presence of coulsonite along the octahedral planes in magnetite, as shown in Figs. 1 and 2, strongly suggests an origin by exsolution of vanadium from magnetite. This shows that only a small amount of

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vanadium may be held in solid solution in magnetite formed under the geochemical environment for this type of deposit. Direct formation of coulsonite, unrelated to any phenomena of exsolution, is shown by single grains and veinlets of the mineral (Figs. 3 and 4). Both of these occurrences must result from the addition of substantial amounts of vanadium and iron to the host rock during the processes of metasomatism.

Conclusions

Coulsonite is a naturally occurring iron-vanadium spinel group mineral with a chemical composition which can be written FeV_2O_4 . Concentrates of this mineral, lacking contamination by ferric iron, show a higher vanadium content than previously reported in the literature for iron spinel minerals.

The mineral may form by exsolution of vanadium from magnetite but also is found separated from magnetite not related to exsolution. The occurrence of this vanadium-rich mineral, separate from but associated with magnetite and confined to igneous metamorphic deposits, supports the idea of the introduction of iron and vanadium into the rock by hydrothermal or pneumatolytic processes.

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