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SCANDIUM CONTENT OF SOME ALUMINUM PHOSPHATES

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ABSTRACT

Scandium is a minor constituent of the aluminum phosphate minerals in the variscite deposit at Fairfield, Utah. The main minerals in the deposit, variscite and crandallite, contain from 0.01 to 0.80 weight percent Sc_2O_3. Comparable amounts are present in millisite, wardite, "deltaite", goyazite and other less common species. A scandium phosphate, sterrettite (kolbeckite), also occurs at the locality. The minerals of the deposit have been formed under near-surface conditions by phosphatic groundwaters probably derived by weathering of phosphorites of the overlying Phosphoria formation, from which the Sc and the chief minor elements associated with it, Sr, Y and V, may also have been derived.

Variscite from other deposits in Utah and Nevada also contains significant amounts of Sc. Variscite, wavellite, crandallite, vashegyite and other Al phosphates from localities outside of this region, however, contain Sc only in traces or below the level of recognition.

INTRODUCTION

Scandium, a dispersed element in a geochemical sense, occurs as a trace element or minor component in a wide variety of minerals (Borisenko, 1961). Most of the existing analytical work has been done on minerals formed in the magmatic cycle, in pegmatities or in hydrothermal deposits. The present note reports the Sc content of crandallite, variscite, wavellite and a few other aluminum phosphate minerals that have formed by weathering or by ground water processes (Table 1). The work has centered on minerals from the variscite deposit at Fairfield, Lehii County, Utah.

FAIRFIELD, UTAH

The mineralogy and paragenesis of the Fairfield deposit has been summarized by Larsen (1942). The chief minerals are variscite and crandallite (pseudowavellite). These are associated with alunite, chert, limonitic clay and small to trace amounts of various aluminum phosphates including "deltaite,"[3] millisite, wardite, gordonite, lehiite and other rare species. The deposit is localized in a highly brecciated zone in

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[3] The status of deltaite as a separate species is questionable. The name is used here in reference to specimens identified in the sense of the description by Larsen (1942).

TABLE 1. SCANDIUM CONTENT OF SOME AL PHOSPHATE MINERALS
(Table states number of different specimens in each range)

	Wt. % Sc_2O_3				
	Below 0.0001	0.001 to 0.001	0.001 to 0.01	0.01 to 0.1	0.1 to 1.0
Crandallite					
$CaAl_3(PO_4)_2(OH)_5H_2O$					
Fairfield, Utah	(see text)			*	*
Sulzbach, Bavaria	1				
Thies, Senegal			1		
Florida	1				
Variscite					
$Al(PO_4) \cdot 2H_2O$					
Fairfield, Utah		1	3	5[a]	
Lucin, Utah		1	1	1	
Kelton, Utah				1	
Mercur, Utah	1			1	
Tooele, Utah			1	1	
Eureka, Nevada			1	1	
Manhattan, Nevada				1	
Montgomery Co., Ark.	1				
Messbach, Bavaria	1				
St. Benigna, Bohemia	1				
Metavariscite					
$Al(PO_4) \cdot 2H_2O$					
Lucin, Utah				1	
Vashegyite					
$Al_4(PO_4)_3(OH)_3 \cdot nH_2O$					
Manhattan, Nevada	1				
Zeleznik, Bohemia	1				
Wavellite					
$Al_3(PO_4)_2(OH)_3 \cdot 5H_2O$					
Cartersville, Georgia	1				
Cumberland Co., Pennsylvania	1				
Chester Co., Pennsylvania	1				
Montgomery Co., Arkansas	1				
Llallagua, Bolivia	1				

[a] Includes a bulk sample of variscite nodules.

The quantitative optical spectrographic analyses reported were made on a Baird two-meter grating instrument, using visual comparison with standards on an ARL Comparator. The standards contained spectrographically pure Sc_2O_3 in synthetic matrices approximating to crandallite or to wavellite in composition. The Sc 3353.7, 3359.7, 3368.9 and 3372.2 Å lines were employed. Duplicate spectrographic analyses of the crandallite made by the Research Laboratory, Kawecki Chemical Company, with exchange of independent standards, yielded identical results. X-ray spectrographic analyses made with a LiF crystal, He path, flow proportional counter and pressed mounts, and employing standards similar to those above, yielded satisfactory quantitative results only in the range over 0.05 percent Sc_2O_3 although the level of detection was lower.

TABLE 1—(*Continued*)

	Wt. % Sc_2O_3				
	Below 0.0001	0.001 to 0.001	0.001 to 0.01	0.01 to 0.1	0.1 to 1.0
Frankenberg, Saxony	2				
Dillenberg, Germany	1				
Langenstriegis, Saxony	1				
Barnstaple, England	1				
Millisite					
$(Na,K)CaAl_6(PO_4)_4(OH)_9 \cdot 3H_2O$					
Fairfield, Utah				2	
Thies, Senegal	1				
"Deltaite"					
$Ca_2Al_2(PO_4)_2(OH)_4 \cdot H_2O$ (?)					
Fairfield, Utah			1	2	3
Wardite					
$NaAl_3(PO_4)_2(OH)_4 \cdot 2H_2O$					
Fairfield, Utah				2	2
Thies, Senegal	1				
Overite					
$Ca_3Al_8(PO_4)_8(OH)_6 \cdot 15H_2O$					
Fairfield, Utah				1	
Gordonite					
$MgAl_2(PO_4)_2(OH)_2 \cdot 8H_2O$					
Fairfield, Utah				1	
Montgomeryite					
$Ca_4Al_5(PO_4)_6(OH)_5 \cdot 11H_2O$					
Fairfield, Utah	1				
Lehiite					
$(Na,K)_2Ca_5Al_8(PO_4)_8(OH)_{12} \cdot 6H_2O$					
Fairfield, Utah				1	
Goyazite					
$SrAl_3(PO_4)_2(OH)_5H_2O$					
Fairfield, Utah		(see text)			1
Paravauxite					
$FeAl_2(PO_4)_2(OH)_2 \cdot 8H_2O$					
Llallagua, Bolivia	1				
Alunite					
$KAl_3(SO_4)_2(OH)_6$					
Fairfield, Utah	2				
Tolfa, Italy	1				
Marysvale, Utah	1				

limestone and was formed at shallow depths. The variscite was formed by phosphatic groundwaters, probably derived by the weathering of overlying phosphorite beds of the Permian Phosphoria formation, now eroded, that reacted with aluminous material in the country rock. The variscite was subsequently more or less altered to crandallite by ground waters of changing composition. This stage was accompanied and followed by the deposition of the rare aluminum phosphates by sequential replacement or as tiny crystals in small cavities and openings.

The Fairfield deposit has close analogies to the so-called aluminum phosphate zone formed by the alteration and leaching of land pebble phosphorites of the Bone Valley formation in Florida (Altschuler *et al.*, 1956). Here, acid phosphatic groundwaters have reacted with clays to form crandallite, millisite and wavellite, with the silica released by the reaction appearing as chert.

The Fairfield crandallite contains Sc over a range of 0.01–0.80 weight percent Sc_2O_3. The content of the Sc varies in successive zones of the crandallite alteration rims around nodules of variscite. It also varies both with the location of the crandallite in the deposit and, somewhat erratically, with the occurrence of the crandallite as nodules or as earthy to dense aggregates. Individual specimens were found to contain 0.2 to 0.8 percent Sc_2O_3, but the bulk of the material[4] ranges between 0.03 and 0.15 percent Sc_2O_3. This content is comparable to the level of enrichment found in better known host minerals for Sc such as wolframite, cassiterite, beryl and allanite.

The Sc determinations on the minerals cited in Table 1 were made on pure samples obtained by handpicking or by heavy liquid separation. In the case of crandallite, there is usually a concentric zonal structure in the crusts and nodules of such dimensions that the zones can not be sampled separately. The variation in the Sc content of successive zones was investigated by electron microprobe scans made on polished thin-sections.[5] The Sc content was found to vary in the zones from virtually nil up to

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[4] The initial analyses of crandallite were based on an extensive collection of specimens made by the late Edwin Over and by one of the authors (A.M.) in the period 1937–1939 at Fairfield. With the recognition of the presence of Sc, the deposit was reopened early in 1959 and a considerable amount of mining was done to determine the distribution and tenor of Sc. A shipment of 330 pounds of crandallite nodules, that averaged 0.14 weight percent Sc_2O_3, was shipped in 1959 to the Kawecki Chemical Company of Boyertown, Pennsylvania, to develop a refining technique. This was followed by a shipment of approximately 4000 pounds of crude ore, containing crandallite with variscite, chert and limonitic clay, that averaged 0.10 weight percent Sc_2O_3. The bulk of the Sc was extracted as Sc_2O_3 in a pilot plant operation utilizing ion exchange resins in the final purification.

[5] The writers are indebted to Mr. Marco Einaudi, of the Department of Geological Sciences, Harvard University, for these measurements.

approximately 0.80 weight percent Sc_2O_3. The Sc content is constant within a particular zone, but varies erratically from zone to zone with a tendency for higher values in the inner zones. In one section, successive zones from a few tenths of a millimeter to over one millimeter thick contained inwardly: 0.12, 0.0, 0.0, 0.05, 0.20, 0.0, 0.33 to 0.84 in a heterogeneous band, 0.58, 0.38 and 0.46 weight percent Sc_2O_3. Inclusions were found in the crusts, using electron back-scatter display (Fig. 1), of a mineral containing approximately 40 weight percent Sc_2O_3. These inclusions probably are sterrettite.

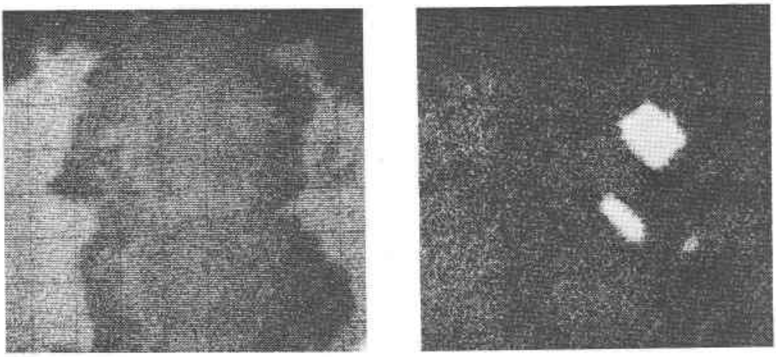

FIG. 1. *Left:* Electron microprobe back-scattered electron display of zones in a crandallite nodule; area about 160×160 microns in size. *Right:* Same area showing Sc Kα display. Light regions ~40 percent Sc_2O_3 (sterrettite inclusions); gray regions ~0.8 Sc_2O_3; black regions ~0.4 Sc_2O_3.

In the course of this work, the supposed Al phosphate sterrettite, originally described from Fairfield by Larsen and Montgomery (1940), was identified by Mrose and Wappner (1959), using specimens supplied by us, to be scandium phosphate, $Sc(PO_4) \cdot 2H_2O$, identical with kolbeckite (and eggonite). The theoretical content of Sc_2O_3 in sterrettite (kolbeckite) is 39.2 percent. The mineral is rare in the deposit and appears to be confined to a particular horizon. Goyazite, a mineral not hitherto reported from Fairfield, was identified during the present study by X-ray study. A bulk sample of crystallized goyazite was found on complete chemical analysis by wet methods to contain 0.30 percent Sc_2O_3.

The crandallite appears to contain, on average, more Sc than the variscite from which it in large part has been derived. Some of the late-formed aluminum phosphates, particularly wardite and deltaite (both with >0.50 percent Sc_2O_3 in some instances) and goyazite, also are relatively rich in Sc. The scandium phosphate sterrettite (kolbeckite) is one of the last-formed minerals. This seeming enrichment in Sc during the sequence of formation of the minerals of the deposit may be related to the chemical processes by which the earlier-formed minerals were re-worked rather than to the introduction of Sc from an outside source by later groundwaters.

OTHER LOCALITIES

A number of variscite deposits apparently similar to Fairfield occur in Utah and Nevada (Sterrett, 1909, 1910, 1911; Pepperberg, 1911). Specimens from some of these localities were examined in the present study and were found to contain significant amounts of Sc (Table 1). The variscite from the well-known localities in Arkansas, Bavaria and Bohemia contains only trace amounts of Sc. Wavellite from all of the nine localities examined contains Sc only in traces or below the level of recognition. The crandallite from Florida, where it occurs as a weathering product of phosphorite, also virtually lacks Sc.

TRACE ELEMENTS ASSOCIATED WITH SC

The principal accessory elements present in addition to Sc are Sr, Y, Ga and V. A number of semiquantitative analyses were made for Sr (X-ray and optical spectrography) and for Y and Ga (optical spectrography). In addition to these elements, undetermined trace amounts were variously found of Cr, Ti, Zr, Sn, Cu, Mn, B and rare-earths.

Sr is the most abundant of the trace elements present in the Fairfield deposit. It is concentrated in crandallite, deltaite and goyazite. Crandallite was found to contain from 0.15 to approximately 1.80 percent SrO in the 20 samples analyzed. An average sample of numerous crandallite nodules contained 0.57 percent SrO (gravimetric). Deltaite was found to contain from 0.20 to approximately 1.90 percent SrO. Goyazite ideally contains 22.5 percent SrO. The content of Sr in wardite, millisite, overite, montgomeryite, englishite and lewistonite was relatively low, below 0.2 percent SrO. Variscite and gordonite contain Sr only in traces.

Y, like Sr, follows Ca. It was present in the range 0.0X Y_2O_3 in a few specimens of crandallite and deltaite from Fairfield. Most speciments of these minerals, however, including a bulk sample of crandallite nodules, contained 0.00X Y_2O_3. A large amount, in or possibly over the range 0.X Y_2O_3, was found in the crandallite from Sulzbach, Bavaria. Y was either present in traces or below the level of detection in variscite and wavellite from all localities. Other rare-earths, particularly La in the Fairfield minerals, also were observed.

Ga, present in substitution for Al, varies widely in amount. It was found in the range 0.0X Ga_2O_3 in some specimens of crandallite, wardite, deltaite and variscite from Fairfield, but most specimens from these and other localities contained 0.000X Ga_2O_3. The content of Ga in wavellite was uniformly low, from a trace to undetected. Alunite from Fairfield contained 0.0X Ga_2O_3, but the Marysvale material contained only a trace.

The V is undoubtedly present in substitution for P.

Analyses for V and other trace elements in variscite and crandallite from Fairfield have been cited by Foster and Schaller (1966), and 0.03 percent Sc_2O_3 has been reported in crandallite from this locality (Vlasov, 1966).

DISCUSSION

The Sc content of the aluminum phosphate minerals listed in Table 1 varies by a factor of over 1000. Structural differences between the various host minerals may be a factor, but the main controls doubtless are in the conditions of formation. The largest differences in the content of Sc are found between different localities for the same mineral, as with variscite and crandallite. All of the minerals from Fairfield are relatively high in Sc, although with some variation associated with the sequence of deposition. This variation presumably is connected with the chemistry of the groundwaters that effected transportation, especially their pH, and with the content of Sc in the source materials from which the solutions derived their content of dissolved material.

The relatively high content of Sc in variscite from Fairfield and other localities in Utah and Nevada contiguous to the present or former extent of the Phosphoria formation is suggestive in this connection. The bulk chemical composition and the trace element content of the phosphorites of the Phosphoria formation has been described by Gulbrandsen (1966), who found from <0.0005 to 0.003 percent Sc, with most values near 0.001 percent Sc, in all of 61 analyses. Ross and Rosenbaum (1962) found up to 0.05 percent Sc in phosphatic shales from Fairfield. The Phosphoria formation also has a noteworthy content of Sr (0.1 percent), Y(0.03 percent) and V (0.03 percent), in addition to other trace elements. The black shales in the Phosphoria formation have a much higher content of V. These elements all are significant constituents of the Fairfield minerals. This falls in line with the view of Larsen (1942) that the mineral content of the groundwaters that formed the Fairfield deposit were derived by weathering of the Phosphoria formation. Summary accounts and bibliographies of the extensive work on the geology and mineralogy of the Phosphoria formation are given by Mansfield (1927) and McKelvey *et al.*, (1959). The presence of Sc in phosphorites in the USSR has been noted by Polyakova (1963) and by Dominikovski and Librovich (1957).

The role of Sc during weathering and in the groundwater cycle is not well understood. The general solution-chemistry of Sc under geological conditions has been discussed by Shcherbina (1959), and the leaching of Sc during the weathering of wolframite and allanite has been described by Kalenov (1958).

The simple Sc^{3+} ion probably does not exist as such in solution. Although a stronger base than Al, the somewhat amphoteric nature and the usual sixfold coordination of Sc^{3} lead to the well-known tendency of this ion to form complexes of considerable stability. These include complexes such as $[Sc(H_2O)_6]^{3+}$ and $[Sc(H_2O)_5OH]^{2+}$ in aqueous solution, and complex ions containing (SO_4), (CO_3) or F. The alkali compounds formed with these complex ions are more or less soluble in water although with a tendency to hydrolyze or to form insoluble basic salts. There are no inorganic reagents that quantitatively precipitate Sc from solution under a wide range of conditions. The most effective precipitants are, in general, phosphate ion and polynuclear anionic complexes containing phosphorus. The action of phosphate ion as a precipitant for Sc under geological conditions is indicated by the mineralogy of the Fairfield deposit, and by the enrichment of Sc in phosphatic skeletal material in sedimentary clays and sandstones (Borisenko, 1961).

At Fairfield, the presence of alunite in the deposit suggests transportation in acid solutions containing sulfate as well as phosphate ions. The sulfate also could be provided by the Phosphoria formation, which locally contains pyrite and has as its major constituent (80 percent) a sulfatic variety of apatite with up to 3.1 percent SO_3. The controlling factor in any case has been the deposition of the aluminum phosphate phases, which through substitution for Al have acted as a co-precipitant or carrier for the Sc^{3+}. Although there is no direct evidence that the Sc^{3+} is present in solid solution in substitution for Al in these minerals, this is indicated by the close crystallochemical relations that exist between Sc^{3+} and (Al,Fe^{3+}) in various natural and synthetic materials (Ito and Frondel, 1968; Frondel, 1968).

The occurrence of Sc at Fairfield has points of geochemical similarity to its known presence in the sandstone-type uranium ores of the Colorado Plateau region (Rose and Roesnbaum, 1962).

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