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RELATION OF IONIC RADIUS TO STRUCTURES OF RARE-EARTH PHOSPHATES, ARSENATES, AND VANADATES*

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Several investigators have reported data on the crystal structures of rare-earth phosphates (Carron and others, 1958), arsenates (Strada

and Schwendimann, 1934; Durif and Forrat, 1957), and vanadates (Milligan, Watt, and Rachford, 1949; Durif, 1956). For each of these groups of compounds, the boundary between the xenotime structure (zircon type, tetragonal) and other structural types is at a different element of the rare-earth group. Most of the investigators failed to note that the rare-earth elements which formed compounds other than of the xenotime type invariably produced compounds isostructural with monazite (monoclinic).

The purpose of this work is to assemble the available data and to correlate crystal structures of the rare-earth compounds with the ionic radii of the trivalent elements and the anions.

By wet chemical methods, we have produced rare-earth phosphates, arsenates, and vanadates that were found by x-ray powder diffraction patterns to be isostructural either with monazite or xenotime. In the arsenate system, we confirmed the study by Durif and Forrat (1957) who showed $SmAsO_4$ to be of the xenotime structure. They stated that $NdAsO_4$ had a different structure which, however, they did not identify. We found $NdAsO_4$ to be isostructural with monazite. In the vanadate system we also confirmed the work of Milligan, Watt, and Rachford (1949) who produced their compounds by igniting equimolecular mixtures of the rare-earth oxides and ammonium metavanadate and reported the vanadates of praseodymium through lutetium to be of the xenotime structure. Durif (1956) reported that $CeVO_4$, prepared by oxidation of "$CeVO_3$", had the xenotime structure. We also prepared $CeVO_4$ by adding a solution of ammonium metavanadate to a solution of cerous chloride and digesting the solution overnight on a steam bath. The compound, dried at 100° C., was found to be isostructural with xenotime. Neither of the investigators cited above noted that only $LaVO_4$ has the monazite structure. Carron and others (1958) have shown that in the phosphate system $TbPO_4$ ($Tb^{3+} = 0.93$ Å) has the xenotime structure whereas its preceding neighbor $GdPO_4$ ($Gd^{3+} = 0.97$ Å) has the monazite structure. Among the actinides, $PuPO_4$ ($Pu^{3+} = 1.08$ Å) has been shown to have the monazite structure (Bjorklund, 1957). With regard to scandium, we found that $ScPO_4$, prepared in a bomb at 300° C. from solutions of $ScCl_3$ and dilute phosphoric acid, and $ScVO_4$, prepared by igniting Sc_2O_3 and V_2O_5 at 1000° C., has the xenotime structure. We also prepared a hydrated scandium arsenate from solutions of $ScCl_3$ and dilute arsenic acid which was isostructural with the metavariscite group of minerals. On ignition this compound assumed the xenotime structure.

Table 1 is a compilation of all of the anhydrous rare-earth phosphates, arsenates, and vanadates, showing the limiting elements for the monazite and xenotime structures in each system. It shows that the xenotime

TABLE 1. STRUCTURES OF RARE-EARTH AND SCANDIUM PHOSPHATES, ARSENATES AND VANADATES

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	Sc
Ionic radius, Å (Ahrens, 1952)	1.14	1.07	1.06	1.04	1.00	0.98	0.97	0.93	0.92	0.92	0.91	0.89	0.87	0.86	0.85	0.81
PO_4	M	M	M	M	M	M	M	X	X	X	X	X	X	X	X	X
AsO_4	M	M	M	M	X	X	X	X	X	X	X	X	X	X	X	X¹
VO_4	M	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X²

¹ From $ScAsO_4$ which was precipitated from solution and ignited by Meeker burner.
² From ignition of a mixture of Sc_2O_3 and V_2O_5 for 8 hours with Meeker burner.
M =Monazite; X =Xenotime.

structure can accommodate increasingly larger cations as the size of the anion increases. There is a quantitative relationship between the radius of the largest xenotime-forming rare-earth element and the size of the anion, in the following manner (formal sixfold coordination radii from Ahrens, 1952):

	P-O	As-O	V-O
A = Oxygen-central atom distance, Å	1.75	1.86	1.99
B = Radius of the largest rare-earth element forming the xenotime structure, Å	.93(Tb^{3+})	1.00(Sm^{3+})	1.07(Ce^{3+})
A/B	1.88	1.86	1.86

The A/B ratio of 1.86 seems to specify the size limits of both the cation and anion at the xenotime-monazite structural boundary. This ratio would lead to the prediction that among orthosilicate compounds (formal Si-O distance of 1.82 Å) the largest cation radius permissible for the xenotime structure would be 0.98 Å. This predicted radius is very close to that of quadrivalent uranium (0.97 Å), and $USiO_4$, coffinite, with the xenotime structure has been synthesized recently (Hoekstra and Fuchs, 1956). Quadrivalent thorium (1.02 Å) which is only 0.04 Å larger than the predicted size forms an orthosilicate with either the monazite or xenotime structure.

Isomorphous substitution of the anions among the rare-earth phosphate, silicate, arsenate, and vanadate systems seems to be possible. However, analyses of xenotime and monazite reported in the literature (Palache and others, 1951) indicate possible replacement of only SiO_4 for PO_4. Although there are no known rare-earth arsenate or vanadate minerals, it might be well in future analyses of rare-earth phosphates and silicates to test for the possible presence of small amounts of arsenic and vanadium.

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GOETHITE-HEMATITE RELATION—AN ORE MICROSCOPE OBSERVATION

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To the south of Chaibasa (22°33′:85°28′), Singhbhum, India, near the northern limit of the Kolhan basin, the fracture zones formed by post-Kolhan deformation, have been mineralized by a metalizing solution. The mineralization is more common in the competent sandstone than in the shale, and also along the sandstone-shale boundary. The mineralizing solution was ferriferous in the first phase and formed such minerals as limonite, goethite and specularite, these being followed by a phase of formation of the manganese minerals psilomelane, pyrolusite, and its idiomorphic form. The important textural relations are the core and rim replacement of goethite by psilomelane, and an intergrowth relation between fibrous goethite and hematite. The latter texture is described in this note.

Such a specimen of goethite on analysis shows a higher content of Fe_2O_3 (91.3%), than normal, because of the included hematite plates.[*]

The intergrowth has been studied on different polished surfaces with respect to the fibre axis. Goethite, the host mineral under reflecting microscope is greyish with perceptible differential adsorption in some specimens, being brighter parallel to the fibre axis. Unusual for goethite, the bireflectance is very weak but with the commoner orange internal reflection. These properties are variable since they depend on the content of adsorbed water (Ramdohr 1955). The mineral is stained brown by $SnCl_2$ ($1\frac{1}{2}$ minute). The reflectance measured in green light in air is 19.3% parallel to the fibre axis and 17.5% across. Specimens polished perpendicular to fibre axis shows no notable variation in reflecting power.

Hematite inclusions occur as continuous plates within the host. In

[*] The planes of hematitization are actually micro S-planes produced by a post-Kolhan deformation, the pattern of which is being studied in this laboratory.