Uranium distribution in pseudowollastonite slag from a phosphorus furnace

By Edward Young and Zalman S. Altschuler

Trace Elements Investigations Report 615

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Geology and Mineralogy

This document consists of 17 pages.
Series A.

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

URANIUM DISTRIBUTION IN PSEUDOWOLLASTONITE SLAG FROM A PHOSPHORUS FURNACE*

By

Edward Young and Zalman S. Altschuler

February 1956

Trace Elements Investigations Report 615

This preliminary report is distributed without editorial and technical review for conformity with official standards and nomenclature. It is not for public inspection or quotation.

---

*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

USGS - TEI-615

GEOLOGY AND MINERALOGY

Distribution (Series A)	No. of copies
Atomic Energy Commission, Washington	2
Division of Raw Materials, Albuquerque	1
Division of Raw Materials, Austin	1
Division of Raw Materials, Casper	1
Division of Raw Materials, Denver	1
Division of Raw Materials, Ishpeming	1
Division of Raw Materials, Phoenix	1
Division of Raw Materials, Rapid City	1
Division of Raw Materials, Salt Lake City	1
Division of Raw Materials, Spokane	1
Division of Raw Materials, Washington	3
Exploration Division, Grand Junction Operations Office	1
Grand Junction Operations Office	1
Technical Information Service Extension, Oak Ridge	6
U. S. Geological Survey:	
Fuels Branch, Washington	1
Geochemistry and Petrology Branch, Washington	20
Geophysics Branch, Washington	1
Mineral Deposits Branch, Washington	1
P. C. Bateman, Menlo Park	1
A. L. Brokaw, Grand Junction	1
N. M. Denson, Denver	1
V. L. Freeman, College	1
R. L. Griggs, Albuquerque	1
W. R. Keefer, Laramie	1
A. H. Koschmann, Denver	1
R. A. Laurence, Knoxville	1
L. R. Page, Washington	1
Q. D. Singewald, Beltsville	1
A. E. Weissenborn, Spokane	1
TEPCO, Denver	2
TEPCO, RPS, Washington, (including master)	2
	60

CONTENTS

ILLUSTRATION

TABLES

URANIUM DISTRIBUTION IN PSEUDOWOLLASTONITE SLAG FROM A PHOSPHORUS FURNACE

By Edward Young and Zalman S. Altschuler

ABSTRACT

Silicate slag from the Victor Chemical Company phosphorus furnace at Tarpon Springs, Fla., has been found to consist essentially of pseudowollastonite, α-$CaSiO_3$. The first-formed crystals are euhedral laths which form a mesh making up most of the slag. As the slag continues to solidify, its composition changes slightly and more equant, subhedral crystals of pseudowollastonite are deposited within the framework of the earlier material. Finally, anhedral masses of fibrous, poorly crystallized material are deposited in the remaining pore spaces which are not always completely filled. Spherules of iron phosphide, Fe_2P, occur very sparsely in the slag as inclusions from the immiscible iron phosphide melt. Uranium content increases in the later crystal products of the slag, and by heavy-liquid fractionation it has been possible to segregate partially the phases and to obtain a fourfold concentration of uranium in 5 percent of the material and a twofold concentration in 30 percent of the material. Nuclear-emulsion studies indicate that the last phases of the silicate slag are actually eight times as radioactive as the early phases. In addition, the iron phosphide spherules are comparably enriched in uranium.

INTRODUCTION

Appreciable tonnages of high-grade uraniferous phosphate pebble composed of apatite are annually smelted electrically for the production of elemental phosphorus. In view of the inevitable mobilizing of uranium during the melting and reduction of the apatite, it is of interest to study the distribution of uranium among and within the resulting products.

The phosphorus furnace operation is essentially the reduction of the calcium fluophosphate--apatite--by electric heating in the presence of quartz with the resultant production of elemental phosphorus and calcium silicate slag. If iron is present in the phosphate rock in more than minor quantities, an iron phosphide slag is formed which is immiscible with the calcium silicate slag.

It has been known for some time that the calcium silicate slags from furnaces using Florida phosphate are approximately as radioactive as the "feed" rock. Accordingly a study by the U. S. Geological Survey was undertaken of the petrography and uranium content of such slag on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission. The authors are indebted to the Victor Chemical Company for supplying samples from their furnace at Tarpon Springs, Fla., and to Mr. James A. Barr, Jr., of the Atomic Energy Commission, for arrangements to obtain the samples and for beneficial interest in the course of the studies.

The material studied is gray, has a vitreous luster, and is massive, except for a fine vesicularity caused by holes less than 1 mm in diameter. Its bulk specific gravity is approximately 2.90. It is made up of felted masses of laths in subparallel orientation showing flow textures. Bronze- to silver-colored metallic spherules, as much as 2 mm in diameter, are sparsely distributed throughout, but such inclusions of iron phosphide may not be typical of the silicate slags.

The aims of the study were to identify the mineral phases present, to establish their uranium contents, and to see if any of the uranium could be preferentially concentrated. To accomplish this a representative sample of the slag was analyzed chemically for the total U and P_2O_5 content; another sample was ground and fractionated by heavy liquids, and the various fractions were analyzed chemically and spectrographically and were studied optically and by X-ray. In addition, thin sections of the slag were studied for optical and petrographic information, and autoradiographic studies of thin sections were made to study uranium distribution.

OPTICAL AND PETROGRAPHIC DESCRIPTION

In thin-section examination it is seen that approximately 65 percent of the material consists of crystal laths in subparallel orientation within small areas. Neighboring masses (or areas) are disoriented with respect to each other and the total effect is a random distribution, particularly as the average lath is about 0.1 by 0.2 by 0.9 mm in size. The crystals are colorless at all orientations under the microscope and show medium to strong birefringence. The laths are biaxial positive, although some of them show only slight separation of the isogyres. In others 2V ranges up to 15°. The laths are of positive elongation and show parallel extinction. They are apparently orthorhombic. The indices of refraction ($\underline{n}_{Na}$) for grains with largest 2V are:

$$\alpha = 1.604 \pm 0.002$$

$$\beta = 1.608 \pm 0.002$$

$$\gamma = 1.650 \pm 0.002$$

The long laths, which constitute the most euhedral pseudowollastonite, form an interlocking meshwork within which the remaining material has crystallized (fig. 1). These laths are obviously the earliest formed crystals in the slag.

The remaining material, which constitutes about 35 percent of the slag, consists of a weakly birefringent material and a brown, almost isotropic material. The weakly birefringent grains are colorless, positive, and apparently uniaxial, with slight or no separation of the isogyres. Most of the crystals show symmetrical extinction; a few, however, show slight departures from symmetrical extinction and some of these exhibit polysynthetic twinning. Indices of refraction are:

$$\epsilon = 1.600 \pm 0.005$$

$$\omega = 1.595 \pm 0.005$$

This weakly birefringent material generally occurs as equant grains not exceeding 0.1 mm on a side. The grains are frequently embayed and invaded by a later phase. The material forms about 25 percent of the slag.

The brown nearly isotropic material makes up 10 percent of the slag. It occurs as anhedral patches of fibrous aggregates and is the last phase to be deposited. It fills cavities within the framework of other crystals and also fills fractures within other phases. It has a mass index of refraction of 1.61, and in habit as well as optical properties is unlike other natural or artificial pseudowollastonites (McLintock, 1932; Rigby, 1948; Winchell, 1946). The indices of refraction of single fibers are unobtainable as almost all the brown material has reacted with or invaded the weakly birefringent material and is intimately dispersed in or associated with this earlier phase. Figure 1 illustrates the mode of occurrence of this end-phase material.

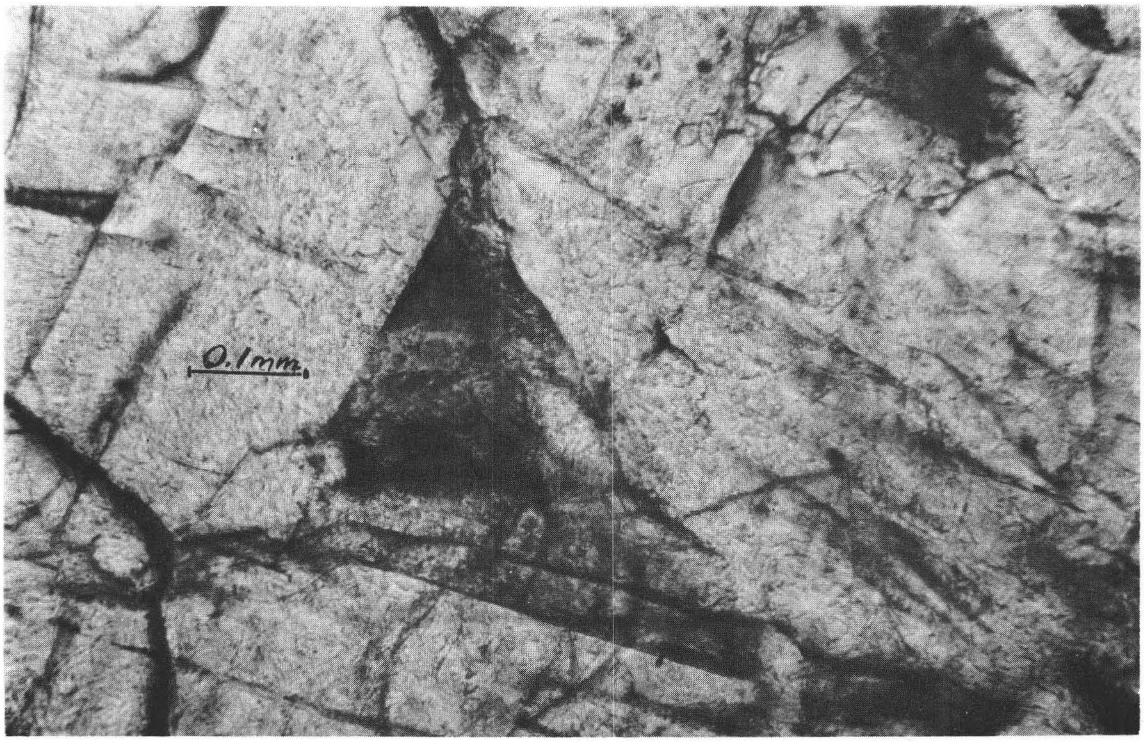

Figure 1.--Photomicrograph illustrating pseudowollastonite of early and late crystallization. The dark triangular patch in the center is a deposit of fibrous end-phase material in a cavity created by the bounding laths of earlier pseudowollastonite. The dark patch in the upper right-hand corner illustrates the manner in which the fibrous material fills fractures in the earlier phase.

ANALYTICAL DATA

The slag contained an average of 1.2 percent P_2O_5 and 0.018 percent U. Most, if not all, of the P_2O_5 is attributed to the iron phosphide (Fe_2P) spherules.

A representative sample of approximately 7 g of the slag was crushed and sized to -200+325 mesh and gravity-processed in acetylene tetrabromide liquids of specific gravity 2.96, 2.98, and 3.10.

Because of the interlocking pattern of crystallization in the slag and the fact that the last phase has reacted with and embayed earlier phases it was impossible to disaggregate the slag into a series of discrete, homogeneous fractions. In addition, the changes in composition, as revealed by the optical inhomogeneity within each fraction and the differences in the spectrographic and X-ray results among the fractions (see below), are evidence of the impossibility of obtaining homogeneous fractions even if it were possible to disaggregate the rock without crushing. Hence the three fractions obtained were mixtures and their composition is given in table 1.

Table 1.--Crystal-phase content of specific-gravity separates.

Fraction	Specific gravity	Lathlike pseudowollastonite (percent)	Equant pseudowollastonite (percent)	Fibrous material (percent)
A	< 2.96	90	10	--
B	2.96-2.98	45	30	25
C	2.98-3.10	10	50	40

everything else is pseudowollastonite, α-$CaSiO_3$,1/ or a closely related compound. Optical data and the lack of uniformity in specific gravity indicate, however, that the pseudowollastonite is not homogeneous. X-ray powder diffraction study of the whole slag shows a mixture of two patterns and X-ray patterns of the specific-gravity separates differ from one another.

The patterns differ by slight shifts in line spacing and by changes in relative intensity; however, the general configuration of the peaks is similar, although not identical, in all patterns. These differences are shown in table 3 for a characteristic group of spacings.

Table 3.--Partial X-ray data on specific-gravity fractions A, B, and C. (CuKα = 1.5418 A; d-spacings in A units)

Reference pseudowollastonite (ASTM card 2-0506)		Fraction A		Fraction B		Fraction C	
d	I	d	I	d	I	d	I
3.41	20	3.427	45	3.427	25	3.427	10
3.22	100	3.243	90	3.243	100	3.243	20
3.04	5	3.058	30	3.058	30	3.058	80
2.81	80	2.797	70	2.814	60	2.858	60

As noted in table 1, the three fractions are mixtures. In the X-ray pattern of fraction B a small peak at 2.797 A appears satellitically on the 2.814 peak, and in the C fraction the 2.858 peak is broadened in a manner indicating the possible presence of the 2.814 peak.

1/ Pseudowollastonite, α-$CaSiO_3$, is the high-temperature phase of $CaSiO_3$.

The patterns for A and B are essentially the same as the patterns of standard pseudowollastonite. The pattern for C was compared with patterns of wollastonite, whitlockite (β-tricalcium phosphate) and CaO, any of which could possibly occur under the conditions of formation of the slag; however, it was found to differ significantly from all of these.

In study of the petrography of the slag, it is apparent that various parts of it have crystallized at different times. It seems reasonable to suppose, therefore, that the differences in X-ray patterns reflect minor differences in the phase crystallizing as the composition of the melt changed during the course of crystallization. In this connection it is interesting to note that the pattern for fraction B is slightly different from that of A and that the significant change in spacing of pattern C is a continuation of the slight change between B and A. (See the shift in d values from 2.797 to 2.814 to 2.858 from A through C.) Moreover, semi-quantitative spectrographic analysis reveals a progressive change in composition that is also most pronounced in fraction C.

Spectrographic analysis

Table 4.--Minor and major element distribution in specific-gravity fractions A, B, and C. Analyst: K. E. Valentine, U. S. Geological Survey.

Percent	A	B	C
Over 10	Ca Si [1]	Ca Si	Ca Si
5 - 10			Al
1 - 5	Mg Al	Al Mg	Mg
0.5 - 1	Na	Na	Na
0.1 - 0.5	Fe K	Fe K	Fe K Mn

[1] The order of precedence indicates greater percent content. Thus, in fraction A, there is more calcium than silicon and more iron than potassium.

Of interest in the data of table 4 is the progressive increase in Al from fraction A to C. Rankin and Wright (1915) in studying the system $CaO-SiO_2-Al_2O_3$ found that a great variety of compounds in binary and ternary eutectic mixtures were obtained with minor variations among the initial oxides, None of the compounds they described has been identified in the slag by X-ray, however, and it seems more likely that as the melt changed in composition during its crystallization the later phases in equilibrium with the melt changed by solid solution. This is demonstrated by the progressive nature of the changes obtained in the X-ray patterns. Nevertheless the changes in structure and composition in fraction C are of sufficient magnitude to indicate that the fibrous material is no longer pseudowollastonite but a somewhat allied substance containing minor aluminum.

In view of the mode of occurrence of the fibrous material as an end-phase product which embays earlier phases, it is difficult to discount the possibility that it may be in part glassy or contain associated glass.

Autoradiographic study

Radioactivity distribution within the slag was also studied by means of nuclear emulsions which had been exposed to thin section of the slag for a three-month period. Cover glasses coated with film specifically sensitive to alpha particles were used, after a design by L. R. Stieff and T. W. Stern (personal communication). Discrete concentrations of alpha tracks from uranium minerals which are otherwise undetectable or from uranium dispersed in a nonuranium host mineral can be observed from the study of such exposed thin sections. By counting the tracks of alpha particles emitted by the thin section the uranium contents of the various mineral phases may be inferred.2/

The nuclear emulsions were studied at high magnification and it was found that uranium was randomly distributed although the uranium content differed among the three major phases. In other words, no discrete centers of unusual alpha activity were found, although the average track density varied. The only exception to this was a concentration of alpha tracks around an iron phosphide spherule. A comparison of the activity in the pseudowollastonite phases and the fibrous material is given in table 5 presenting the actual counts obtained from three typical areas in the thin section.

2/ This presupposes that the content of thorium and its daughter products is insignificant, an assumption that is borne out by the previous Th analyses on Florida phosphorites and the lack of convergent four- and five-track clusters in the recording emulsion. If present, thorium should produce four- and five-branch stars from Th^{228} (Senftle et al., 1954).

Table 5.--Alpha-track distribution in pseudowollastonite slag.

Slag phase	Total α-tracks counted	Area surveyed (in mm^2)	Activity in α/mm^2	Activity in α/mm^2/day
Lathlike pseudowollastonite, moderately birefringent	21	0.048	438	4.8
Weakly birefringent pseudowollastonite	76	0.072	1056	11.5
Fibrous end-phase material	71	0.024	2960	32.2

These data corroborate the findings from chemical analysis of the gravity separates. The analyses showed a fourfold enrichment between the lightest and the heaviest fractions. The enrichment in alpha activity between early lathlike pseudowollastonite and the late fibrous material is eightfold. The gravity fractions, however, were not pure with respect to mineral phases as was shown in table 1, and the differences between the chemical analyses and the alpha counts perhaps reflect the difference between the recovery that can be obtained and the enrichment that actually prevails.

CONCLUSIONS

Two approaches for selectively concentrating uranium in the slag are suggested by the above studies.

Spectrographically it was found that the fibrous end-phase material is characterized by more aluminum than the two pseudowollastonite phases. In view of the much greater uranium content of the fibrous material, an increase in its total quantity could lead to an appreciable increase in the total amount of uranium taken up from the melt by this phase. Addition of excess aluminum to the furnace charge may augment the production of fibrous material and thus lead to such an increase in the amount of uranium segregated in a single phase.

Another manner of effecting enrichment is suggested by the anomalous concentration of uranium in the iron phosphide spherules. Normally the iron phosphide liquid segregates immiscibly from the silicate liquid and the resultant iron phosphide slags have been found to contain little uranium.[3] This is not merely due to relative dilution, as much less iron phosphide is produced than calcium silicate. Evidently the uranium is retained in the calcium silicate liquid. The unusually high uranium contents of the iron phosphide spherules suggest, therefore, that iron phosphide remaining in contact with the silicate liquid phase can scavenge uranium. It may thus be possible to concentrate uranium by addition of iron, or iron and phosphorus, to the calcium silicate fraction, after the silicate and phosphide liquids have separated.

In view of the enrichment of uranium in the late-stage liquors of the melt it is suggested that segregation of these liquors may yield a concentration of uranium, which, if amenable to extraction, may become a valuable byproduct of the elemental phosphorus industry.

---

[3] Personal communication, James A. Barr, Jr., U. S. Atomic Energy Commission.

REFERENCES

McLintock, W. F. P., 1932, On the metamorphism produced by the combustion of hydrocarbons in the Tertiary sediments of south-west Persia: Mineralog. Mag., v. 23, p. 207-226.

Rankin, G. A., and Wright, F. E., 1915, The ternary system $CaO-Al_2O_3-SiO_2$: Am. Jour. Sci., 4th ser., v. 39, p. 1-79.

Rigby, G. R., 1948, Mineralogy of ceramic materials, The British Refractories Research Association, 179 p.

Senftle, F. E., Farley, T. A., and Stieff, L. R., 1954, A theoretical study of alpha star population in loaded nuclear emulsions: Geochim. Cosmochim. Acta, v. 6, p. 197-207.

Winchell, A. N., 1946, Elements of optical mineralogy, 3d ed., pt. 2, New York, John Wiley and Sons, p. 403.