ANALYSES OF THE MINOR CONSTITUENTS IN POLLUCITE

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Abstract

Three specimens of pollucite (Greenwood, Maine, U.S.A.; Tin Mountain, S. Dakota, U.S.A.; and Varuträsk, Sweden) have been examined qualitatively for Pb, Sn, In, Ag, Cb, Y, La, Sr, Ba, W and Be and quantitatively for Rb, Tl, K, Li and Ga, using the spectrograph.

From the available data it appears that Rb and Tl are enriched in pollucite to a considerable extent. The mean Rb_2O content is 0.53% (seven analyses) and the mean Tl_2O content is 0.0028% (five analyses).

The mean weight ratio Rb_2O/Tl_2O is 150 (five ratios), which is very similar to the mean ratio of about 110 in potassium minerals, indicating that Rb^+ and Tl^+ replace Cs^+, and K^+, with the same relative facilities.

In general the spectra of the different specimens of pollucite indicate that the mineral is relatively free from the presence of several of the rarer elements commonly found in pegmatitic minerals. A trace of strontium was found in each specimen of pollucite; the quantity of strontium present in each case suggests that it is largely radiogenic.

A brief outline is given of the qualitative method of analysis.

Introductory

Shortly after publishing quantitative analyses of the minor constituents in two specimens of pollucite (Ahrens, 1), three more specimens of this rare and fascinating mineral were very kindly sent by Dr. Michael Fleischer of the U. S. Geological Survey. After cleaning each mineral from possible sources of contamination, the specimens were examined qualitatively and quantitatively using the spectrograph, and the results of the analyses are given and discussed in this paper.

Analytical

(*a*) *Qualitative analysis:*

Several of the rarer elements were sought which are frequently found in pegmatitic minerals, particularly in those which have been formed from later residual emanations. These elements were:

Pb: All feldspars and several specimens of mica that have been examined contain Pb; other investigators have reported the presence of Pb in feldspar.

Sn: Many specimens of muscovite and lepidolite have been found to contain Sn.

In: This rare element has been detected in about fifteen per cent of the muscovite and lepidolites that I have examined.

Ag: Many specimens of feldspar and also of mica contain traces of silver.

Cb: Cb is invariably found in granite, probably entering the mica lattice, and this element has been found in all lepidolites (0.005–0.2% Cb_2O_5), and some muscovites that have so far been analysed by the author. Although tantalum is invariably associated with columbium and is found in mica (Rankama, 2), it was not sought because its spectral sensitivity is extremely poor.

Y, *La*, *Be*, *W:* All are relatively common in pegmatites.

Sr: Strontium was sought because its presence was expected as a result of the radioactive decay of rubidium, relatively large quantities of which may be found in pollucite.

Ba: The presence or absence of barium would serve as a rough indicator as to the genesis of strontium.

For the analyses of lead, tin, silver and indium (volatile elements in the arc) a low amperage was employed (2–3 amps) and only the first minute of arcing was recorded. For the detection of the relatively involatile elements such as columbium, yttrium, lanthanum, strontium, barium and beryllium, each specimen of pollucite was treated with hydrofluoric acid and the residue taken to dryness, prior to arcing. All fluorides are readily volatilised from the arc: this renders the detection of traces of the involatile elements more sensitive and simple than by analysing without prior acid treatment, even if care has been exercised to arc the untreated mineral to completion so as to record the spectra of the involatiles.

Each fluoride residue was arced for 30 seconds at 6–7 amps, and in each case the mineral was volatilised from the anode.

Figure 1 shows the spectrum of pollucite fom Karibib (see Ahrens, 1) which had been treated with hydrofluoric acid. Sr 4077 is very clearly evident and its intensity may be contrasted with the extreme weak in-

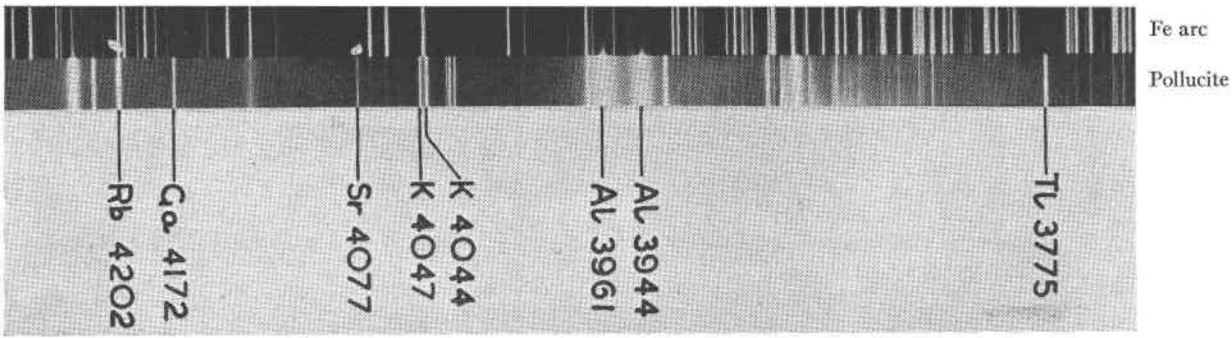

FIG. 1. Spectrum of residue of a specimen of pollucite (Karibib, South West Africa) after treatment with hydrofluoric acid. Note strong relative intensities of Sr 4077 and Al $\begin{cases}3944\\3961\end{cases}$ compared with the weak intensities of these lines in Figure 2. It is probable that the emission of Sr 4077 is from radiogenic strontium (Sr^{87}).

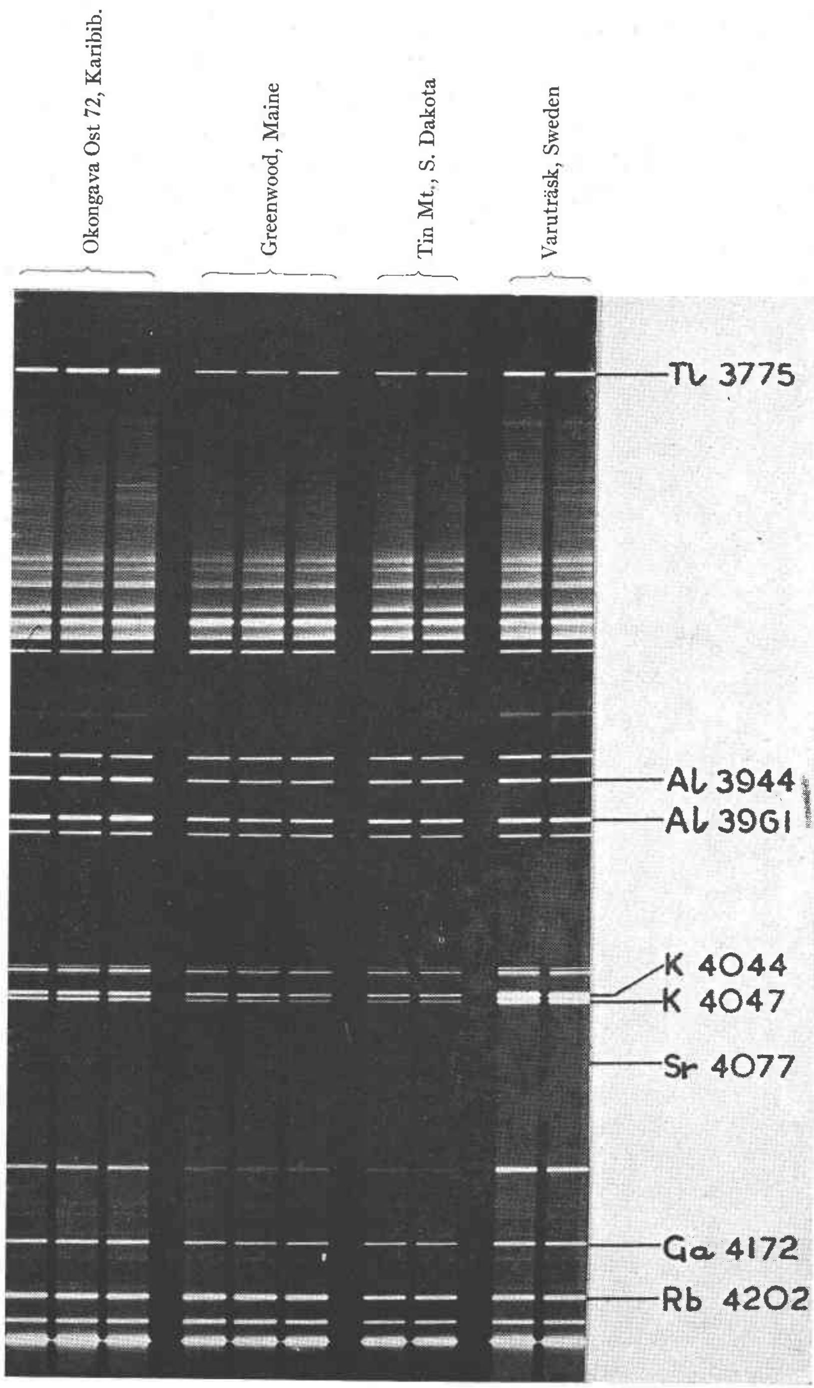

FIG. 2. Duplicate and triplicate spectra of different specimens of pollucite. The presence of gallium, potassium, rubidium and also the rare element thallium, several properties of which are similar to the alkali metals of higher atomic weight, is clearly evident in each case.

tensity of Sr 4077 in the different spectra on Figure 2. Note also the difference in intensities between Al$\begin{cases}3944\\3961\end{cases}$ on Figure 1 (relatively intense) and on Figure 2 (relatively faint); Al is relatively involatile when silicates are arced, but by conversion to the fluoride it is made volatile.

A blank examination on the hydrofluoric acid failed to reveal the presence of any of the elements sought.

(*b*) *Quantitative analysis:*

A specimen of pollucite from Karibib, the analysis of which was known (Ahrens, 1), served as a standard for the estimation of gallium (semi-quantitative), thallium, rubidium, potassium and lithium. A description of the quantitative spectrochemical technique for estimating Rb and Tl is described in the literature (Ahrens, 3) and a similar method may be employed for the estimation of potassium and lithium. Figure 2 shows the spectra of the different specimens which have been arced in duplicate or in triplicate; inspection of this Figure shows that agreement between the duplicate and triplicate analyses is reasonably close in each case.

Results and Discussion

(*a*) *Qualitative:*

Of all the elements sought qualitatively, Sr alone could be detected, and was present in all three specimens. In this respect the spectrum of pollucite is relatively "pure" when compared with the spectra of other pegmatitic minerals and one probable reason for this purity is that the lattice of pollucite does not contain a site capable of accommodating medium size ions, that is, ions in six-fold co-ordination as in mica, for example.

The presence of traces of strontium will be discussed under a separate sub-heading (Radioactivity of rubidium).

(*b*) *Quantitative:*

The quantitative results are given in Table 1.

Table 1

Locality	%Tl_2O	%Rb_2O	%K_2O	%Li_2O	%Ga_2O_3
Greenwood, Maine, U.S.A.	0.0019	0.68	0.16	0.008	0.0005
Tin Mt., S. Dakota, U.S.A.	0.0019	0.25	0.19	0.006	0.0005
Varuträsk, Sweden	0.0080	0.37	2.5	0.053	0.0010

The results of these analyses will be discussed under three sub-headings.

(1) *Abundance of rubidium:*

Including the three analyses given in this paper, seven analyses of rubidium in pollucite are now available, and these are given in Table 2.

TABLE 2

Locality	$\%Rb_2O$	Author
Tin Mt., Black Hills, U.S.A.	absent	Wells & Stevens (4)
Tin Mt., Black Hills, U.S.A.	0.25	Ahrens (This paper)
Norway, Maine, U.S.A.	0.23	Ahrens (1)
Greenwood, Maine, U.S.A.	0.68	Ahrens (This paper)
Karibib, S.W. Africa	0.54	Ahrens (1)
Varuträsk, Sweden	0.37	Ahrens (This paper)
Varuträsk, Sweden	1.60	Quensel (5)

With the exception of the first analysis, these analyses indicate that rubidium is relatively enriched in pollucite which appears to contain about the same quantity as is commonly found in green microclines (amazonite). For analyses of rubidium in amazonite, see Goldschmidt (6), Tolmacev, (7) and Ahrens (3).

After lepidolite, which is the mineral richest in rubidium, pollucite (and amazonite) appears to be richest in rubidium, although relatively large quantities may on occasion also be encountered in muscovite and biotite.

It is surprising that Wells and Stevens were unable to detect any rubidium in their specimen from Tin Mountain.* They analysed their specimen chemically for the alkali metals and examined different alkali metal rich fractionates spectroscopically and in each case rubidium was found to be absent.

(2) *Abundance of thallium:*

Five analyses of thallium in pollucite are now available; three in this paper and two in the previous publication (1), and the mean Tl_2O content of these five analyses is 0.0028%. This value is about the same as the mean Tl_2O content of fifteen amazonite specimens, which is 0.0023% (3).

* Their specimen was not the same one as that analysed by me.

Together with amazonite, pollucite is probably the mineral second richest in rubidium, lepidolite being the richest.

(3) *Ratio Rb_2O/Tl_2O:*

The mean weight ratio Rb_2O/Tl_2O in potassium minerals is about 110 (3) and the limits of variation of this ratio are 30 (minimum) and 650 (maximum). In pollucite where Rb^+ and Tl^+ replace Cs^+ instead of K^+ as in potassium minerals, the Rb_2O/Tl_2O ratios of five specimens that have been analysed are:

Greenwood	350	This publication
Tin Mt.	130	
Varuträsk	45	
Karibib	50	Previous publication on the minor constituents in pollucite (1).
Norway (Maine)	180	

The mean ratio for these five specimens is 150 and is very similar to the mean ratio for the potassium minerals. Because the Rb_2O/Tl_2O ratios are about the same for potassium minerals and for pollucite, there is little doubt that Rb^+ and Tl^+ replace K^+, and Cs^+, with the same or very nearly the same relative facilities.

(*c*) *The presence of strontium and the radioactivity of rubidium:*

In the earlier publication on pollucite (1) it was suggested that the presence of a trace of strontium in the Karibib pollucite could be ascribed to the radioactive disintegration of rubidium; $Rb^{87} \rightarrow \beta$ particle $+ Sr^{87}$. Hahn and co-workers (8) have isolated strontium from a specimen of pollucite, examined it on the mass-spectrograph, and found Sr^{87} predominant with only a very small amount of $Sr.^{88}$ The results of the analyses of the specimens described in this paper corroborate the above evidence that Sr in pollucite is largely radiogenic, because in each of the three specimens of pollucite traces of strontium could be detected; furthermore, although no accurate estimates of the strontium contents were made, approximate determinations showed that in each case the quantity of strontium was about equal to that expected, if it were radiogenic. Thus, although the specimen of pollucite from Maine contained 0.68% Rb_2O, whereas the specimen from Tin Mountain contained 0.25%, the strontium content of the former appeared to be slightly less than that of the latter. This is in agreement with the relative ages of the two specimens in question; the age of the specimen from Maine is about 300,000,000 years (from Sr/Rb measurements on lepidolites), whereas the age of the pollucite from Tin Mountain is very much greater, and is probably about 1,300,000,000 years, as determined from Pb/U ratios of uranium minerals from the Black Hills. (A preliminary note on the use of Sr/Rb ratios for age determinations has been published (9) and a detailed account is in the press.)

In none of the specimens could barium be detected (limit of detection about 0.0001% Ba); this absence of barium provides indirect corroborative evidence of the radiogenesis of strontium.

Acknowledgments

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