QUANTITATIVE SPECTROCHEMICAL EXAMINATION OF THE MINOR CONSTITUENTS IN POLLUCITE

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Contents

Abstract

Details are given of a quantitative spectrochemical analysis for Tl, Rb, Li, Ga, and K, in two samples of pollucite, one from Karibib, South West Africa, and the other from near Norway, Maine, U.S.A., and the presence of these elements (excluding potassium) within the pollucite lattice is discussed.

The ratio, Rb/Tl, is approximately 50 (Karibib) and 180 (Maine). Both ratios are within the limits of 40 and 440 found in 42 analyses of various Rb- and Tl-containing minerals, chiefly South African, data on which will be published later. Although the former ratio (50) is considerably lower than the mean ratio of the 42 analyses (150) it is worth noting that the mean Rb/Tl ratio for two samples of lepidolite from the same locality was found to be almost identical (70), providing further evidence that Rb and Tl enter different crystal lattices with equal facility.

The presence of a trace of strontium is discussed, and a radioactive origin, involving the transition $Rb^{87} \rightarrow Sr^{87}$, is suggested.

Introduction

Recently, a sample of pollucite from Karibib, South West Africa, was examined at the Union Geological Survey, South Africa, by Nel.[1] This investigation included a qualitative spectrochemical analysis by Dr. B. Wasserstein, who detected, apart from certain other elements, Tl, Rb, Li, and Ga.

The author has been engaged on research on the geochemistry of thallium, gallium, and the three rare alkali metals, and included in this research was the development of a quantitative spectrochemical technique for their estimation in rocks and minerals. In view of the paucity of analytical data concerning these elements in rocks and minerals, and since, to the knowledge of the author, no analyses exist for thallium, rubidium, and gallium, in pollucite, it was decided to employ the spectrochemical method for a quantitative examination.

Another sample of pollucite from Maine, U.S.A., was kindly placed at the author's disposal by Professor T. W. Gevers of the Geology Department, Witwatersrand University. Unfortunately, only a very small uncleaned piece was available for analysis, so that this sample cannot be regarded as truly representative. However, for one important object of this investigation, that is the determination of the ratio Rb/Tl, the extreme purity of the sample is not of much significance.

In the chemical analysis of the pollucite cited by Nel[1] the potassium and rubidium contents are reported together as mixed oxides; hence it was decided to analyse quantitatively for potassium as well.

EXPERIMENTAL

Details of the spectrochemical technique for the analysis of the above elements in rocks and minerals, together with the underlying principles, will appear in the press at a later date; suffice it to say that the method depends primarily on the volatility of the alkali metals in the arc, using anode excitation and a low amperage. As a result of the ease with which the alkali metals volatilise in the arc, the first fraction of vapours volatilising when rocks, etc., are analysed, consists predominantly of sodium and potassium. Certain other elements, including thallium and gallium (to a lesser extent) also volatilise very readily. The method consists essentially of exposing only the alkali metal rich fraction, on the assumption that under these conditions the effects of extraneous elements are annulled, whence the method may be applied to various rocks and mineral types.

With the assistance of standards containing fifteen per cent of a 1:1 mixture of potassium and sodium carbonates, and using microphotometric measurements, the unknowns are determined.

When pollucite is analysed, the predominant vapour in the arc during the early stages of arcing is caesium, followed by silicon and then aluminium. An argument that might thus be levelled against the method is that in the case of the synthetic standards, a sodium-potassium vapour is predominant in the arc gas column, while in the case of pollucite, the vapour is predominantly that of caesium. Since one important factor influencing the intensities of lines is the composition of the arc gas column, a comparison of line intensities produced on the one hand in a potassium-sodium vapour, and on the other, in a caesium vapour, would at first sight appear to incur difficulty. However, since the alkali metals possess low ionisation potentials, when in quantity they all produce a cooling effect, and furthermore, since the values of these ionisation potentials are similar, it is reasonable to assume that unless extreme accuracy is desired, the line intensities may be readily compared, irrespective of whether the predominant vapour is caesium or potassium+sodium.

Needless to say, the prepared synthetic standards which contained varying amounts of thallium, rubidium, lithium, and gallium, could not be utilised for the estimation of potassium, for whose determination certain carefully analysed rocks were used as standards.

RESULTS

Table 1 provides the mean values of the analyses, carried out in triplicate.

TABLE 1. QUANTITATIVE ANALYSES OF POLLUCITE

	% Tl_2O	% Rb_2O	% Li_2O	% Ga_2O_3	% K_2O
Karibib	0.011	0.54	0.021	0.0012	0.49
Maine	0.0013	0.23	—	0.0012	0.76

The lithium content of the sample from Maine could not be determined as a result of the extreme density of the lithium line. Since this sample had not been cleaned and since lithium minerals are commonly associated with pollucite, an analysis would have been of no value.

In the case of the Karibib sample, chemical analysis returned a figure of 1.3% Rb_2O+K_2O, all calculated as Rb_2O. If the above K_2O content is calculated as Rb_2O and added to the Rb_2O found, a total of 1.5% is obtained, which is in reasonably good agreement with the chemical result of 1.3%.

DISCUSSION

Before providing a brief discussion on the occurrence of Tl, Rb, Ga, and Li, in pollucite, a short account will be given of certain salient factors underlying the formation of this caesium mineral, in contrast with the fact that no discrete mineral is formed by the commoner rare alkali metal, rubidium.

Residual phases of differentiation are commonly relatively rich in ions of large dimensions, in accordance with the fact that when two (or more) ions of slightly different sizes, but of like valency, compete for a similar site within a given growing lattice, the smaller ion is generally more acceptable, the larger ion being relatively enriched in the mother liquor fraction. Thus we find Cs^+, Rb^+, and Tl^+, all ions of large dimensions, continually rejected during differentiation and enriched in the residua of differentiates. The degree of enrichment will depend to a large extent on the relative radii of the ions in question, the larger the ion the greater the degree of enrichment.

The radius of Cs^+ is greater than that of Rb^+ and Tl^+ (its radius is greater than that of any other ion), with the result that when caesium, rubidium, and thallium substitute for potassium, which they invariably do, in potassium rich minerals ($K^+=1.33$, $Rb=Tl=1.49$ and $Cs^+=1.65$Å), since Cs^+ is the largest ion, it is acknowledged with relatively greater reluctance than Rb^+ and Tl^+. The result is that caesium tends to concentrate relatively to rubidium and thallium in the residual differentiates. Thus, although rubidium is considerably more abundant than caesium in the earth's crust (Atomic ratio Rb/Cs=approx. 50), no rubidium mineral has ever been reported resulting from differentiation, whereas, as a result of the relatively greater enrichment of the larger caesium ion, this less abundant element does on occasion form the caesium mineral, pollucite.

(*1*) *Rubidium and Thallium*

Since rubidium and thallium behave in approximately the same manner as caesium during differentiation, the presence of relatively appreciable quantities of these two elements in pollucite is to be expected. Furthermore, since the radii of Rb^+, Tl^+, and Cs^+, are of the same order, Rb^+ and Tl^+ undoubtedly occur in substitutional solid solution replacing Cs^+.

From Table 1, the ratio Rb/Tl is 50 (Karibib) and 180 (Maine). The former ratio is somewhat less than the average ratio of about 150 found in 42 analyses of various minerals, although it lies within the extreme limits of 40 and 440 found in these analyses. Analyses of two lepidolites from the same locality (Karibib) also revealed low Rb/Tl ratios. Table 2 provides the mean results of the analyses of these two samples.

TABLE 2. QUANTITATIVE ANALYSIS OF LEPIDOLITE

% Tl_2O	% Rb_2O
0.021	1.60

In this case the ratio Rb/Tl is 70, which to all intents and purposes can be regarded as being equal to the ratio for pollucite, when taking into account slight regional variations and experimental errors.

Apart from the fact that the ratios in both samples of pollucite fall within the limits of 40 and 440, this constancy of the ratio Rb/Tl in two entirely different minerals from the same locality, provides an interesting confirmation of what has been concluded from the results of the 42 analyses mentioned above, and that is: excluding those phases where thallium enters sulfide minerals, rubidium and thallium comprise a pair of elements, remarkable in the constancy of their relative proportions, this constant relationship apparently being independent of the mineral type and holding over all ranges of concentration. The essential underlying factors determining this constant relationship is that both Rb^+ and Tl^+ are monovalent ions, the radii of which are identical.

(2) *Gallium*

The presence of gallium in almost all aluminium-rich minerals is now well established as a result, chiefly, of the work of Goldschmidt and Peters,[2] Al^{+++} (radius=0.57Å) being replaced by Ga^{+++} (radius=0.62Å). The ratio Al/Ga is, however, by no means constant and varies very considerably even when only taking into account Al silicate minerals of igneous origin. It is a little surprising to find only 0.0012% Ga_2O_3 in both samples of pollucite, since gallium tends to concentrate relatively to aluminium as a rule, in residual phases. The gallium content of the lepidolite from Karibib is twenty times as much as that of the pollucite (0.025% Ga_2O_3). A relatively high gallium content appears to be characteristic of lepidolites and also muscovites.

It is not quite clear why pollucite is poor in gallium, although Goldschmidt has pointed out that the chemical characteristics, chiefly the pH, of the solutions play a very important part in influencing the Al/Ga ratio, which is apparently in delicate balance.

(3) *Lithium*

Although Li is a relatively small ion (radius 0.78Å) it is also rejected during differentiation and tends to concentrate in late pegmatitic phases, together with the other rare alkali metals and thallium. However, the reasons for this rejection are different from those outlined for the late enrichment of the large ions. Although Li^+ is capable of replacing Mg^{++} and Fe^{++} in the ferromagnesian lattices (Mg^{++}=0.78, Fe^{++}=0.83Å) it is not readily accepted, probably as a result of the monovalency of the lithium ion and its resultant weak attraction, relative to the divalent ions. Lithium cannot be accommodated, either in the plagioclase or potash feldspars, or in quartz, since none of these mineral structures contain ions in sixfold co-ordination. Micas do contain small amounts of lithium, which is only to be expected, since one essential feature of the structure of the mica lattice is that it includes sites for ions capable of sixfold co-ordination. However, probably as a result of the monovalency of lithium, ions of higher potential enter the earlier micas preferentially. For these reasons, lithium is present in quantity in only very late differentiates (Li micas and other lithium minerals). As is to be expected, pollucite is commonly associated with lithium minerals.

As a result of this association it is not surprising to find a small quantity of lithium in pollucite. However, whether the lithium is present in small amounts of lithium minerals as impurities, or not, cannot be definitely established. The Karibib sample had been carefully cleaned and we may therefore assume that at least part of the lithium occurs within the pollucite lattice itself. It is extremely unlikely that lithium is capable of replacing Cs, although Nel has suggested a mechanism whereby Cs^+ is replaced by $Na^+ + H_2O$. In a like manner $Li^+ + H_2O$ might be capable of replacing Cs^+. It should also be borne in mind that pollucite possesses a lattice, the structure of which is fairly open and which, unlike the more closely packed types, is possibly conducive to considerable interstitial movement of ions, particularly small ones like Li^+. It is therefore quite likely that part of the lithium is held within the pollucite lattice in interstitial solid solution.

RADIOACTIVE DISINTEGRATION OF RUBIDIUM

Both potassium and rubidium are naturally radioactive, their radioactivity being characterised by the emission only, of beta particles. By losing a beta particle, the rubidium isotope of mass number 87 is transformed into a strontium isotope of equivalent mass number. (It is believed that only Rb^{87} is radioactive.) It is thus possible that the strontium contained in certain minerals is essentially that of mass number 87, that is, derived from the radioactivity of rubidium. For example, Mattauch[3] has been able to establish, by means of mass spectra, that the strontium present in a rubidium-rich mica from Canada is predominantly that of mass number 87, ordinary strontium being present in only negligible traces.

If we assume the half life period of rubidium to be 2.3×10^{11} years, and the age of the later phases of the Old Granite of South Africa, in which the Karibib pollucite occurs, to be approximately 9.0×10^{8} years, then the amount of strontium that would have accumulated from 0.54% Rb_2O during this period is 0.0014%.

A careful spectrochemical examination of the Karibib pollucite, necessitating arcing to completion as a result of the very late appearance of the strontium spectrum, revealed definite traces of strontium. Unfortunately a quantitative method for determining the strontium content was not at hand, although an approximation could be made, which indicates that the strontium is present in quantities greater than 0.001%, but less than 0.004%, thus suggesting a radioactive origin. Another factor which suggests a radioactive origin for the strontium is the absence of barium. Thus, although strontium and barium do not constitute a coherent pair of elements in the same sense as do rubidium and thallium, they are nevertheless invariably associated. Furthermore, since the radius of Ba^{++} is greater than that of Sr^{++} (1.43 and 1.27Å, respectively), there is often a tendency for Ba^{++} to concentrate relative to Sr^{++} in later phases of differentiation. However, as the barium concentration is below the limit of detection (below about 0.0001% Ba), this further suggests that the genesis of the strontium in the Karibib pollucite may be ascribed to the radioactivity of rubidium.

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