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Molecular Spectroscopic Evidence of the Existence of Strontium Isotopes Sr^{88}, Sr^{87}, and Sr^{86}

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An analysis of certain heads of the sequence $v'-v''=+1(^2\Sigma\rightarrow{}^2\Sigma)$ in SrF arc emission spectra, revealed three components at each of the first heads, the displacements of which show the presence of three strontium isotopes at masses 88, 87, and 86. A quantitative determination of the abundance ratio, 88/86 gave a value of 8.52, which is in reasonably good agreement (+2.0 percent) with the abundance ratio of 8.38 determined mass spectrographically. The accuracy with which this ratio has been determined is considered to be within ±4–6 percent. Abundance ratios, 88/87 and 87/86 could be determined only approximately because of masking of the $Sr^{87}F$ component by the dominant $Sr^{88}F$ component. The spectra had been recorded using first order (dispersion, 0.848 A/mm), but if second order were used, this masking would be reduced to an insignificant amount. For geological age requirements, mass-spectrographic measurement of strontium isotope abundance ratios is preferable because as little as 0.3 mg of strontium salt is required, whereas using molecular spectra, far larger amounts are required. As the maximum concentration of strontium in the most ancient rubidium-rich minerals does not exceed 0.02 percent, inconveniently large quantities of mineral have to be employed to extract sufficient strontium for a molecular spectroscopic analysis.

1. INTRODUCTION

FOR the determination of geological age, the lead and helium methods are commonly used, but recently the strontium method has also been applied.[1,2] This last method is based on the natural β^--decay of $Rb^{87}\rightarrow Sr^{87}$; if the ratio Sr^{87}/Rb^{87} can be determined in a given mineral, the age of the mineral can be calculated since the decay constant of the transmutation is known. In a spectrochemical or chemical analysis the ratio $Sr(total)/Rb^{87}$ can be estimated, and since primary (ordinary) strontium will be present in the mineral to a greater or lesser extent, relative abundance measurements have to be made of the strontium isotopes.

The common procedure is analysis by means of the mass spectrograph. This procedure is well adapted to strontium, but it was decided to explore other possible methods for showing and estimating different strontium isotopes. In the field of optical spectroscopy, Heyden and Kopfermann[3] have been able to show the presence of the three main strontium isotopes in common strontium and the presence of Sr^{87} only, in radiogenic strontium, by a hyperfine structure analysis of certain emission lines of strontium. This paper will describe some investigations that were carried out on molecular spectra.

2. CHOICE OF SUITABLE MOLECULAR SPECTRA

It is well known that molecular spectra are emitted by emitters of the type SrF, SrCl, SrBr, and SrI in flame sources and also in the arc. Spectra emitted by SrF are intense and clearly defined and can be conveniently produced using the common d.c. arc, whereas the other Sr halide spectra tend to be much weaker and diffused in this source because the energies of dissociation of SrI, SrBr and SrCl are much smaller than that of SrF. Furthermore, fluorine has only one isotope, which makes an examination of the spectra for isotope effects much simpler. SrF arc emission spectra were therefore selected to investigate the possibility of showing the presence of strontium isotopes, 88, 87, and 86 and to make relative abundance measurements on these isotopes.

3. EARLIER WORK

An earlier attempt had been made by Harvey[4] to show the presence of Sr^{86} and Sr^{88} by using SrF emission spectra. This author carried out his investigations in 1931, at which time the presence of Sr^{87} was still unknown. Harvey pointed out

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[1] L. H. Ahrens, Trans. Geol. Soc. S. Africa, in press (1947).

[2] L. H. Ahrens, Bull. Geol. Soc. Am., in press.

[3] M. Heyden and H. Kopfermann, Zeits. f. Physik **108**, 232 (1937).

[4] A. Harvey, Proc. Roy. Soc. **A133**, 336 (1931).

that because of the small difference from unity of the isotope coefficient, ρ, for Sr^{88} and Sr^{86}, the detection of isotope heads in the sequence $v'-v''=0$ $(^2\Sigma\rightarrow{}^2\Sigma)$ is not possible, whereas the separation in the squence $v'-v''=+1$ should be of the order of 1 cm^{-1}, that is, about 0.33A at the wave-length of these bands (~5700A). Using a 21-ft grating, Harvey recorded spectra in the 1st order; these spectra showed faint companion heads on the violet side of each main head in the $v'-v''=+1(^2\Sigma\rightarrow{}^2\Sigma)$ sequence. The measured shift, $Sr^{88}F-Sr^{86}F$ was found to be in reasonably good agreement with the theoretical shift as calculated from the equation, $\nu-\nu=(\rho-1)\nu_v$, using 17257 cm^{-1} for the system origin for computing ν_v.

4. PRESENT INVESTIGATION

Since the above investigation was carried out, Sr^{87} has been discovered, and although Harvey's results do appear to indicate the presence of Sr^{86}, they are not conclusive because no indication of the presence of Sr^{87}, which should have been apparent, was evident on his plates. It is quite probable that although the resolving power of the grating was sufficient, dispersion was not sufficient to register three separate isotope components for each head, and consequently in this investigation a greater dispersion has been used (see later discussion).

The isotope coefficients

$$\rho_1=(\mu^{Sr^{88}}/\mu^{Sr^{86}})^{\frac{1}{2}},\quad \rho_2=(\mu^{Sr^{88}}/\mu^{Sr^{87}})^{\frac{1}{2}},$$
$$\rho_3=(\mu^{Sr^{87}}/\mu^{Sr^{86}})^{\frac{1}{2}}$$

are given below. μ = reduced mass, calculated according to the equation $1/\mu=(1/m_1)+(1/m_2)$, where m_1 and m_2 are, respectively, the mass of a given strontium isotope and the mass of F.

$$\rho_1=1.00207,\quad \rho_2=1.00103,\quad \text{and}\quad \rho_3=1.00106.$$

From the values of ρ calculation shows that $Sr^{88}F-Sr^{87}F$ and $Sr^{87}F-Sr^{86}F$ shifts are ~0.5 cm^{-1}, which corresponds to about 0.15A; a minimum resolving power of 40,000 and a large dispersion is therefore necessary to record the individual isotope heads.

A large (35 ft.) Paschen-type grating spectrograph, kindly placed at my disposal by Dean George R. Harrison of the Department of Physics, Massachusetts Institute of Technology, was used. Theoretical resolving power was 180,000 and dispersion 0.848 A/mm, in the 1st order.

A 1:1 mixture of SrF_2 and powdered carbon was placed in a cupped graphite anode and arced, using a d.c. source of excitation run at 6–7 amp. Thirty separate exposures, each of two minutes, were made (total exposure time one hour) and the spectra were recorded on Eastman Type 103-G spectroscopic plates.

Because of the astigmatism of the mounting, emulsion calibration (photographic response *vs.* intensity) could not be made using step weakeners, sectors, etc., and a separate calibration spectrum was made with the aid of a Wadsworth-type grating spectrograph (Cabot Spectrographic Laboratory, Department of Geology, Massachusetts Institute of Technology) using a rotating step sector and an iron arc as source. Calibration and analysis plates were developed under identical conditions.

5. RESULTS

Qualitative

According to Harvey,[4] the heads of the $v'-v''=+1$ sequence are, with the exception of the first two, close doublets, the separations of which increase towards the red. This doublet formation has been found to obscure the measurements of isotope displacements, and measurements could be made only on the first heads. In addition, the appearance of a background—the fine structure of preceding heads—is considerable for all heads with the exception of the first few. The head freest from background interference is the (2,1) head, and accurate displacements and relative intensity measurements could be made. Some measurements were also

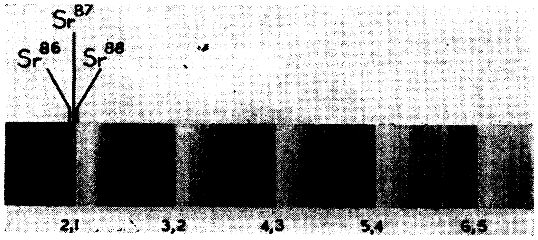

FIG. 1. SrF arc emission spectra of the sequence $v'-v''=+1(^2\Sigma\rightarrow{}^2\Sigma)$. $Sr^{88}F$, $Sr^{87}F$, and $Sr^{86}F$ components are particularly clear in the (2,1) head.

TABLE I.

(2,1) head: $Sr^{88}F = 17771.28\ cm^{-1}$	Calculated shift	Observed shift	
	cm^{-1}	cm^{-1}	A
$Sr^{88}F - Sr^{86}F$	1.06	1.06	0.337
$Sr^{88}F - Sr^{87}F$	0.53	0.52	0.165
$Sr^{87}F - Sr^{86}F$	0.54	0.54	0.172
(3,2) head: $Sr^{88}F = 17959.56\ cm^{-1}$			
$Sr^{88}F - Sr^{86}F$	1.04	1.03	0.326
$Sr^{88}F - Sr^{87}F$ $Sr^{87}F - Sr^{86}F$	Interference excessive.		

made on the (3,2) head, but attempts to measure isotope displacements on the other heads were fruitless because of extensive interference from head doubling and background fine structure. Figure 1 shows the (2,1), (3,2), (4,3), (5,4), and (6,5) heads; the presence of isotope heads may be seen best in the (2,1) heads.

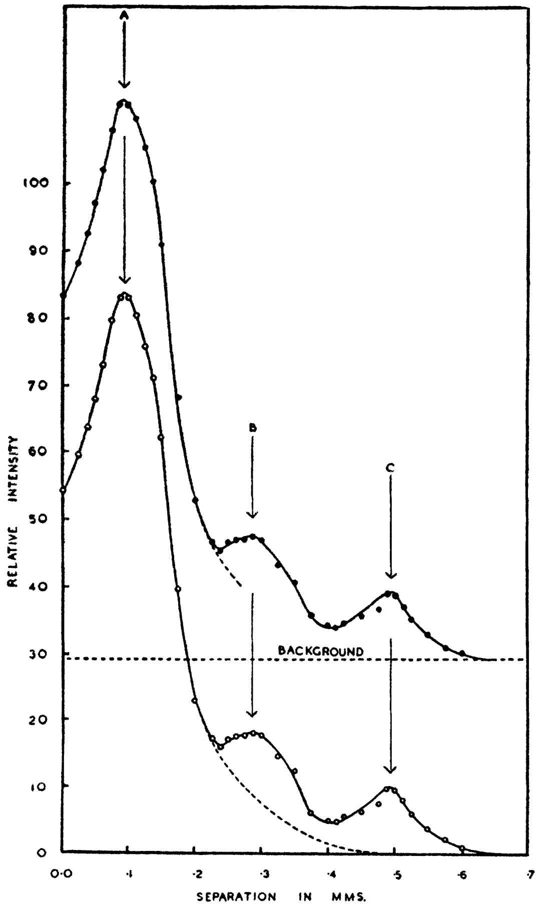

FIG. 2. Microphotometer trace of (2,1) head: $A = Sr^{88}F$ component, $B = Sr^{87}F$ component, and $C = Sr^{86}F$ component.

Band head displacements and intensity measurements were made with the aid of a Hilger non-recording microphotometer. The (2,1) and (3,2) heads were scanned by moving the plate at definite small intervals across the microphotometer light beam falling on the photo-cell and noting the galvanometer deflection at each setting. These deflections were converted to densities and by referring to the calibration curve (density *vs.* log intensity), the photographic response, measured as density, was converted into relative intensity units.

Figure 2 shows a plot of relative intensity (arbitrary units) *vs.* isotope head separation (in mm) for the (2,1) head. The upper curve is not corrected for background, whereas the lower curve has been corrected for background by a subtraction of background intensity from the total intensity at each reading. Three peaks are clearly in evidence, the separation of which could be measured accurately.

In Table I, theoretical and measured isotope displacements are given for the (2,1) and (3,2) heads. The wave numbers of the main ($Sr^{88}F$) heads, have been taken from Harvey.[4]

Because each isotope head in the (3,2) head appeared to be broader than in the (2,1) head, $Sr^{88}F$ masked $Sr^{87}F$ to a considerable extent; consequently, no sharp $Sr^{87}F$ peak could be obtained and hence only the $Sr^{88}F - Sr^{86}F$ displacement for the (3,2) head is given in Table I.

Where it has been possible to make accurate displacement measurements, agreement between calculated and observed results are very close, and the presence of the three peaks in Fig. 2 is due, therefore, to the three strontium isotopes of masses 88, 87, and 86. Another isotope of strontium (Sr^{84}), the relative abundance of which is 0.6 percent, has been found mass spectrographically, but because background and fine structure are relatively intense, the presence of this isotope could not be verified by using molecular spectra. Reference to Fig. 2 shows that for Sr^{86} (relative abundance ~10 percent) background intensity is about three times greater than that of the isotope head alone, and would thus be almost fifty times greater than the intensity of the $Sr^{84}F$ head alone.

Quantitative Relative Abundance Measurements

The relative abundance of the four known strontium isotopes (88, 87, 86, and 84) are, respectively, 82.6, 7.02, 9.86, and 0.56 percent according to mass-spectrographic data.

In Fig. 2, the predominance of Sr^{88} is easily seen and the ratio 88/86 may be determined with reasonable accuracy. Unfortunately, the ratio of 87 to either 88 or 86 could not be measured with precision because of masking of the $Sr^{87}F$ head by that of $Sr^{88}F$. If the spectra are recorded in the 2nd order, accurate measurements on the relative abundance of Sr^{87} could also be made.

From mass-spectrographic data, the abundance ratio $Sr^{88}/Sr^{86}=8.38$ and the ratio determined from molecular spectra is 8.52. Agreement is reasonably close as the difference is only 2.0 percent, but it is difficult to ascertain the accuracy of the latter determination. The experimental error limits are undoubtedly greater than 2.0 percent and are probably about ±4–6 percent.

The approximate ratio Sr^{88}/Sr^{87} was determined as 10.1 (±25 percent), whereas the mass-spectrographic ratio is 11.8. The accuracy with which this ratio could be determined could be increased very considerably by using 2nd-order spectra. However, further investigation on the use of the 2nd order was not continued, partly because of the difficulty with which this wavelength area of the spectrum could be recorded by using the available layout, and mainly because of the greater sensitivity of the mass spectrograph. According to recent investigations by Mattauch,[5] an accurate quantitative mass-spectrographic analysis may be made on as little as 0.3 mg of strontium salt. For these isotope investigations by the use of molecular spectra far greater amounts of strontium are required, and although the sensitivity obtained in this investigation could be enhanced, it would never be nearly as sensitive as the mass spectrograph. This drawback is a serious one for geological age measurements because the minerals on which age determinations are made contain at the most 0.02 percent Sr—usually much less—and consequently inconveniently large quantities of mineral would have to be worked up to produce a sufficient quantity of strontium for a strontium isotope analysis using SrF emission molecular spectra.

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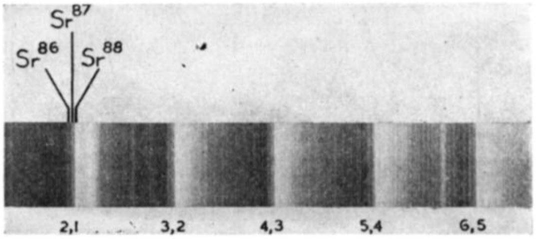
[5] J. Mattauch, Am. angew. Chemie 2, 37 (1947).



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