

## Indication of a Genetic Relation Between Indium and Tin

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Existing data reveal a widespread association of indium with tin in ores of the latter element. This is taken as an indication of a genetic relation, ascribed to a "forbidden" transition of  $\text{Sn}^{115}$  to  $\text{In}^{115}$ .

ISOBARS of adjacent elements of the periodic system (nuclei of equal mass number and unit difference in atomic number) are mutually transformable, in the direction of increasing atomic number by the emission of an electron and a neutrino, and in the reverse direction by the emission of a positron or absorption of an electron, again with emission of a neutrino. The existence of couples of this type in which there is no detectable activity raises at once the question as to whether such species are energetically stable with respect to each other, or whether one member is unstable but of long life. According to the theory of Yukawa and Sakata<sup>1</sup> true stability is possible within a range of mass difference of the atoms of the pair equal to twice the mass of the neutrino. Only if the mass of the neutrino is zero is stability impossible for both members of the pair. But if the neutrino mass, though finite, is very small in comparison with the electronic mass, as the slope near the end point of  $\beta$ -ray distribution curves indicates, occurrence of stable pairs should be very infrequent. The occurrence of apparently stable pairs actually is relatively infrequent,<sup>2</sup> but more common than would be probable on the above basis.

Failure of direct detection of radioactivity in these cases may most probably be ascribed therefore to low rates of transformation. These might result from very small mass differences, from unfavorable spin relationships, or from unfavorable mass differences as far as the  $K$  electrons (which have the highest probability of reaction) are concerned in cases where the only process possible is the absorption of an extra-

nuclear electron by one member of the pair. In the attempt to prove the occurrence of a transformation, resort must then be made to indirect evidence, such as the universal association, or lack of it, of the two members of the pair in minerals of sufficient geological age.

One of the best established examples of the couples in question is found in  $\text{In}^{115}$  and  $\text{Sn}^{115}$ . A rough calculation outlined in the earlier paper<sup>2</sup> indicates the instability of the tin isotope. In the hope of obtaining evidence concerning the transformation, a review of existing data on the mineralogical association of indium with tin has been made, with results outlined below.

Indium occurs associated in small amounts with many other elements, among which tin is often included. Interest centers in the present connection, however, in minerals in which tin is present in large proportion. The earliest data bearing upon this point are found in the work of Hartley and Ramage,<sup>3</sup> who investigated spectroscopically many samples of various ores and minerals. Among these were included five ores of tin, two cassiterites ( $\text{SnO}_2$ ) and one tinstone ( $\text{SnO}_2$ ) from Cornwall, one tinstone from Saxony and one stannite ( $\text{FeCu}_2\text{SnS}_4$ ) of unknown origin. Each of these showed the presence of indium.

The next observations of interest are those of Garrett<sup>4</sup> and Green<sup>5</sup> concerning the presence of indium in metallic tin. Garrett found the element to be present in spectroscopically detectable quantity in all available samples of tin metal, including highly refined samples. Green also investigated a number of samples of the metal, in only four of which indium was not detected. Two of these were highly purified samples, and two less pure of unknown source. These obser-

<sup>1</sup> Yukawa and Sakata, *Proc. Phys. Math. Soc. Japan* **17**, 467 (1935).

<sup>2</sup> This fact, in connection with the assumption that both members of isobaric pairs cannot be stable, was used in an earlier paper (*Phys. Rev.* **46**, 1 (1934), cf. pp. 5, 15) in support of the idea that electron capture is a process of considerable probability in energetically favored cases.

<sup>3</sup> Hartley and Ramage, *J. Chem. Soc.* **71**, 533 (1897).

<sup>4</sup> Garrett, *Proc. Roy. Soc.* **114A**, 289 (1927).

<sup>5</sup> Green, *Nature* **119**, 893 (1927).

vations indicate a widespread occurrence of indium in the ores of tin.

Brewer and Baker,<sup>6</sup> interested in the discovery of richer sources of indium through a study of its association with other elements in minerals, and actuated by the observations of Garrett, carried out a systematic investigation of tin ores. They examined a total of thirteen oxide ores and four sulfide ores. The oxides comprised ten samples of cassiterite, of which seven were from Cornwall and one each from Malay, Bolivia and Tasmania, one sample of Cornish stream tin, noted to be geologically distinct from the tinstones, and two samples, one pegmatite and one alluvial, from Nigeria. The sulfides were cylindrite ( $\text{Pb}_6\text{Sb}_2\text{Sn}_6\text{S}_{21}$ ), franckeite ( $\text{Pb}_5\text{Sb}_2\text{Sn}_2\text{S}_{12}$ ) and teallite ( $\text{PbSnS}_2$ ), all from Bolivia, together with a Cornish stannite. Several of the Cornish cassiterites proved to be of very high purity, and afforded the only examples in which no indication of indium was found. Six of these samples, including the three in which indium was not detected, were obtained from one mining company. The more perfectly crystallized material, presumably occurred therefore together with less pure material which did contain indium. The crystallization process in these cases had evidently taken place under conditions resulting in very complete exclusion of impurities. If the crystallization occurred in relatively recent time, the failure to find indium by the technique employed (which was not intended to be of maximum sensitivity,<sup>7</sup> does not necessarily offset in the present argument the otherwise uniformly established association.

<sup>6</sup> Brewer and Baker, *J. Chem. Soc.*, 1286 (1936).

<sup>7</sup> The percentages of indium when reported as definitely present were usually of the order of 0.001 to 0.01, except in the samples of cylindrite and franckeite, where they were 0.1 to 1.0.

The chemistry of indium and tin is not sufficiently similar to result in frequent association of the type often found with elements of the same periodic group. Tin in its ores is usually tetravalent and indium trivalent. The crystal radii in these valences are about 0.73 and 0.86Å, respectively. These differences in valence and radius of the ions make any significant isomorphism of their compounds unlikely. The latter phenomenon however may well be responsible for the relative enrichment of indium in the complex sulfide ores containing antimony, which is trivalent and no doubt of about the same ionic radius as indium. On the whole, it appears improbable that a chemical segregation of indium with tin is responsible for its presence in the minerals discussed above.

Before complete acceptance of evidence of the kind presented here, further experimental studies designed to discover any relation which may exist between the proportion of indium and tin and the age and history of the ore, and also the proportion<sup>8</sup> of the isotopes of indium in the element obtained from tin ores are desirable. As far as the present evidence goes, however, it indicates a genetic relation of indium to tin, of which the transformation discussed above is the most obvious explanation.

The spin of  $\text{In}^{115}$  is given by Jackson<sup>9</sup> as 9/2. That of  $\text{Sn}^{115}$  is unknown but the species  $\text{Sn}^{117}$  and  $\text{Sn}^{119}$  are assigned by Tolansky<sup>10</sup> a value of  $\frac{1}{2}$ . The transition between  $\text{Sn}^{115}$  and  $\text{In}^{115}$  would seem therefore to be of a strongly "forbidden" type, accounting for its slowness, if it occurs.

<sup>8</sup>  $\text{In}^{115}$  comprises 95.5 percent of the element and  $\text{In}^{113}$  4.5 percent. There are eleven known isotopes of tin,  $\text{Sn}^{116}$  comprising 0.44 percent.

<sup>9</sup> Jackson, *Zeits. f. Physik* **80**, 59 (1933).

<sup>10</sup> Tolansky, *Proc. Roy. Soc.* **A144**, 574 (1934).