History of science

Isotope geochemistry and cosmochemistry

from R. Letolle

ONE hundred years ago, Sir William Crookes (1832–1919) explained at the British Association meeting in Birmingham some of the principles then relevant to problems in geoscience and nucleosynthesis, and argued for the existence of isotopes. Twenty-four years before the conceptualization of isotopes by Soddy, Crookes published the results of his reflections (*Nature* **34**, 423; 2 September 1886), showing an extraordinary prescience of some present-day concepts of isotope chemistry and geochemistry.

In 1911, Soddy had just discovered yttrium, and the intricacy of spectroscopic lines of the mixture of rare-earth elements led him to conclude that elements could be a mixture of some 'meta-elements'. He recalled Prout's system when he wrote:

". . . Let us picture the very beginnings of time, before geological ages, before the Earth was thrown from the central nucleus of the original *protyle.* Let us still imagine that at this primal stage all was in an ultra-gaseous state, at a temperature inconceivably hotter than anything now existing in the visible Universe; so high, indeed, that the chemical atoms could not yet have been formed, being still far above their dissociation point . . ."

From Crookes' Birmingham address, 24 years earlier:

"We require a word, analogous to protoplasm to express the idea of the origin primal matter existing before the evolution of the chemical elements. The word I have ventured to use for this purpose is compounded of πρσ (earlier than) and υλη (the stuff of which things are made). The word is scarcely a new coinage, for 600 years ago Roger Bacon wrote in his *De Arte Chymiæ*: 'The elements are made out of υλη, and every element is converted into the nature of another element'."

Relative to the possibility of unstable atoms and the chemical fractionation of atoms of various masses of the same element, Crookes says:

". . . I have said that the original protyle contained within itself the potentiality of all possible atomic weights. It may well be questioned whether there is an absolute uniformity in the mass of every ultimate atom of the same chemical element. Probably our atomic weights merely represent a mean value around which the actual atomic weights of the atoms vary within certain narrow limits.

Each well-defined element represents a platform of stability connected by ladders of unstable bodies. In the first accreting together of the primitive stuff the smallest atoms would form, then these would join together to form larger groups, the gulf across from one stage to another would be gradually bridged over, and the stable element appropriate to that stage would absorb, as it were, the unstable rungs of the ladder which led up to it. I conceive, therefore, that when we say the atomic weight of, for instance, calcium is 40, we really express the fact that, while the majority of calcium atoms have an actual weight of 40, there are not a few which are represented by 39 or 41, a less

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Royal Society

William Crookes

number by 38 or 42, and so on. We are here reminded of Newton's 'old worn particles'.

It is not possible, or even feasible, that these heavier and lighter atoms may have been in some cases subsequently sorted out by a process resembling chemical fractionation? This sorting out may have taken place in part while atomic matter was condensing from the primal state of intense ignition, but also it may have been partly effected in geological ages by successive solutions and re-precipitations of the various earths.

This may seem an audacious speculation, but I do not think it is behond the power of chemistry to test its feasibility . . ."

After that Crookes presents his own experimental evidence of the reality of various species of yttrium atoms, based on spectroscopic data. In fact, yttrium is monoisotopic, and isotope effects in radiation spectra were discovered experimentally much later. Nevertheless, Crookes' idea is true and he in fact observed the complex array of spectral lines resulting from various rare-earth elements and some of their combinations. Some of his conclusions merit quotation:

"Returning . . . to the idea of heavy and light atoms, we see how well this hypothesis accords with the new facts here brought to light. From every chemical point of view the stable molecular group, yttrium, behaves as an element. Excessive and systematic fractionation has acted the part of a chemical 'sorting Demon', distributing the atoms of yttrium into several groups, with certainly different phosphorescent spectra, and presumably different atomic weights, though all these groups behave alike from the usual chemical point of view. Here, then, is one of the elements the spectrum of which does not emanate equally from all its atoms, but some atoms furnish some, other atoms others, of the lines and bands of the compound spectrum of the element. And as this is the case with one element, it is probably so in a greater or less degree with all. Hence the atoms of this element differ probably in weight, certainly in the internal motions they undergo.

Another important inference which may be drawn from the facts is, that the atoms of which yttrium consists, though differing, do not differ continuously, but *per saltum.* We have evidence of this in the fact that the spectroscopic bands characteristic of each group are distinct from those of the other groups, and do not pass gradually into them. We must accordingly expect, in the present state of science, that this is probably the case with the other elements. And the atoms of a chemical element being known to differ in one respect may differ in other respects, and presumably do somewhat differ in mass.

Restricted by limited time and means, even a partial separation of these atomic groupings is possible only with enormous difficulty. . ."

Coming back to the origin of elements, Crookes discusses at length a theory of element-building from protyle (note that the word υλη was introduced again by Gamow in the 1940s in his theory of the Big Bang) and wonders about the gap between uranium and thorium from lighter elements (in lead). He concludes:

". . . What comes after uranium? I should consider that there is little prospect of the existence of an element much lower than this . . ."

The explanation of the absence of elements between thorium and lead, which refers to the instability of such elements, is ingenious and, in the context of knowledge at that time, is not far from the truth.

There are in this wonderful and forgotten paper many striking ideas on other problems, for instance:

". . . A genesis of the elements such as is sketched out would not be confined to our little Solar System, but would probably follow the same general sequence of events in every centre of energy now visible as a star."

and:

"[it is] . . . a question that I especially commend to the younger generation of chemists, not only as the most interesting, but the most profoundly important, in the entire compass of our science." □

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