Technical Papers

Isotopic Composition of Bromine in Nature

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Relatively few of the chemical elements have been investigated by precision mass spectrometry in the search for variations in isotopic composition in nature. In general only the light elements have been so investigated. The approximately equal abundance of the two bromine isotopes makes precision ratio measurement easier and in addition the sublimation of sodium bromide in a source adapted for solid sample handling eliminates any question of fractionation in a gas handling system.

Elemental bromine for this investigation (*1, 2*) was obtained from four suppliers. Searles Lake bromine, produced by the American Potash Corp., Los Angeles, Calif., is believed to be in large part of volcanic origin. Bromine from Michigan salt brines (Dow Chemical Co., Midland, Mich.) and from West Virginia brines (Westvaco Chemical Div., Food Machinery and Chemical Corp., New York) is considered to be representative of the bromine in Silurian sea water approximately 350×10^6 yr ago. Bromine from Pacific Ocean water was produced by the Westvaco Chemical Div. from salt bitterns at Newark, Calif. The Dow-Ethyl Corp. produces bromine from Gulf water at Freeport, Tex., but does not market it. A sample of ethylene dibromide from this origin was obtained from F. N. Holmes of the Ethyl Corp. Laboratory in Baton Rouge, La.

Portions of the elemental bromine samples were reacted with an excess of ammonium hydroxide in an ice bath, evaporated to dryness, redissolved, and then the calculated amount of sodium hydroxide was added to convert to sodium bromide. The ethylene bromide sample was refluxed in acetone solution with a small excess of sodium iodide. The bromide recovered was contaminated with some sodium iodide. Every attempt was made to secure complete recovery and to avoid possibility of fractionation by partial crystallization. Small rolls of fine nickel screen or fragments of porous Alundum were impregnated with a concentrated aqueous solution of sodium bromide, oven dried and then vacuum dried. These samples were installed in an ion source specifically developed for handling solid samples (*3*).

Measurements were made with two 60° sector spectrometers of 15-cm radius; the bromide vapor was ionized by 75-ev electrons, and 1900-v acceleration potential was used. The ion beams were brought alternately upon the collector by magnetic field scanning. The voltage developed in the input resistor of the FP-54 electrometer was balanced by voltage from a precision decade potentiometer, residual galvanometer deflections being converted into potentiometer readings by interpolation factors determined experimentally. For each ratio reported in Table 1 at least 10 ratio measurements were made. The precisions are stated for each set of data at the 95-percent confidence level. In general two sets of data were taken on each sample some hours apart to verify that no shift with time occurred. Measurements were made over a period of some months whenever instrument time was available.

No significant difference appears to exist among these samples. In addition, there is excellent agreement between the grand average of these determinations and the ratio determined by Williams and Yuster (*4*), which is the value accepted for this ratio by Bainbridge and Nier (*5*):

	Br^{79}/Br^{81}
This measurement	1.0217 ± 0.0002
Williams and Yuster	$1.0210 \pm .0020$

Bromine derived from Dead Sea brine was not available, but might be interesting to investigate, particularly since there is speculation that it may originate from beds of purple snail fossils. No sample of bromine-bearing mineral has been examined. These are rather rare, the silver halide ores probably being the best source.

Table 1. Bromine isotopic ratio in samples of known origin.

Sample origin	$NaBr^{79+}/NaBr^{81+}$	Average
Michigan brines	1.0222 ± 0.0030	
	$1.0256 \pm .0009$	
	$1.0242 \pm .0002$	
	$1.0204 \pm .0007$	
		1.0231 ± 0.0040
Searles Lake	$1.0256 \pm .0020$	
	$1.0241 \pm .0005$	
	$1.0223 \pm .0005$	
	$1.0204 \pm .0006$	
	$1.0200 \pm .0001$	
		$1.0224 \pm .0062$
Pacific Ocean	$1.0202 \pm .0010$	
	$1.0248 \pm .0009$	
	$1.0207 \pm .0007$	
	$1.0160 \pm .0001$	
	$1.0204 \pm .0002$	
	$1.0174 \pm .0031$	
		$1.0214 \pm .0043$
West Virginia brines	$1.0194 \pm .0014$	
	$1.0207 \pm .0007$	
	$1.0205 \pm .0007$	
		$1.0202 \pm .0016$
Gulf water (ethylene dibromide)	$1.0226 \pm .0018$	
	$1.0188 \pm .0025$	
	$1.0205 \pm .0012$	
		$1.0206 \pm .0040$

References and Notes

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1. This article is based on work performed for the U.S. Atomic Energy Commission by the Carbide and Carbon Chemicals Co., a division of Union Carbide and Carbon Corp., at Oak Ridge, Tenn.
2. The recommendations of Ralph Cannon of the U.S. Geological Survey were followed in selecting the samples.
3. A. E. Cameron, "Electron bombardment ion source for mass spectrometry of solids," *Rev. Sci. Instr.*, in press.
4. D. Williams and P. Yuster, *Phys. Rev.* **69**, 556 (1946).
5. K. T. Bainbridge and A. O. Nier, "Relative isotopic abundances of the elements," Preliminary Rept. No. 9, Nuclear Science Series, National Research Council, (NP-1971).

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particularly interesting to biologists that specific reactions are involved in defense [illegible] intimidation when there is little or no display apparent,

Territorialism in Two Species of Salamanders

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Among the vertebrates it is well known that certain activities of individuals of a species may be limited to more or less roughly defined areas or home ranges. Territories may be established in the defense of such areas or portions thereof. Relatively little information is available on the home ranges and territories of the poikilothermal tetrapods. Examples of investigations that have yielded meaningful results are those of Nichols (*1*) on the home range of the box turtle, *Terrapene carolina* and Evans (*2*) on territorial defense in *Anolis sagrei,* the Cuban lizard. The display of aggressive territoriality in the South American frog, *Phyllobates trinitatis* has recently been described by Test (*3*). Aggressiveness was most pronounced in adult females in the defense of their home sites and feeding grounds.

In the urodeles, females of several species are customarily found on or near the developing egg masses. Such a situation has been thoroughly described by Wood (*4*) in the four-toed salamander, *Hemidactylium scutatum*. His investigations seem to indicate that this is not a case of territorialism per se, for the majority of the females present at nesting sites are gravid, having congregated for the purpose of laying eggs rather than maintaining a vigil over them.

This paper reports preliminary studies of territorialism in *Hemidactylium scutatum* and the two-lined salamander *Eurycea bislineata*. Studies were conducted in aquariums provided with a terrain of moss and forest debris in order to simulate the natural habitat of the animals. Each habitat thus established occupied an area 18 by 9 in. In the first experiment four specimens of *E. bislineata* were introduced into this environment. Two individuals immediately selected stations under bark fragments at opposite ends of the area. After a period of several weeks it became apparent that these were permanent stations and it was possible to plot a home range for each individual. This extended for a radius of 5 to 6 in. from the centrally located shelter site except where limited by the walls of the chamber. Repeated experiments, in which as many as six individuals were used, showed that the laboratory habitats described above would support no more than two resident individuals at a time. In almost every case there was a slight overlapping of the home ranges. Although food was supplied throughout the environment, established individuals were observed eating outside their home area on only two occasions. It is reasonable to assume that in this species the home range corresponds roughly to the general feeding grounds.

Animals that did not occupy home ranges wandered at random. When an errant individual entered the home range of another member of its species, it was allowed to approch within 2 in. of the shelter site. At this point the resident advanced and placed its snout in direct contact with that of the intruder. After the antagonists had remained in this posiiton for several minutes, the intruder always backed away from the area and continued its course in a different direction. Such intimidation of the intruder was the usual method of defense displayed by *E. bislineata*. On occasion, however, this technique was abandoned in favor of direct assault, in which the intruder was bitten about the snout or tail, not infrequently losing large portions of the latter member during the foray. These investigations indicate that the actual territory of *E. bislineata* is limited to a region in the immediate vicinity of the shelter site. The undefended portions of the home range cover a considerably larger area.

The number and composition of the home ranges established by *H. scutatum* corresponded closely to those of *E. bislineata*. However, territorialism was not as aggressively maintained as in the two-lined salamander. Intimidation was the only method of defense observed. An intruder usually halted as a resident advanced toward it from the shelter site. Although there was seldom any direct contact between the two animals, the mere presence of the resident seemed to be sufficient intimidation to cause the intruder to withdraw. Intruders were occasionally allowed to pass unmolested over shelter sites. However, since two animals never occupied the same shelter and since no resident was ever evicted from his established domain, it is reasonable to conclude that in *H. scutatum* the integrity of the territory is maintained, although aggressive territorialism is but weakly developed. It is interesting to note that specimens of *H. scutatum* and *E. bislineata* that did not establish a home range consistently refused to accept food under any conditions and eventually starved to death.

Territorialism has been observed in *E. bislineata* and *H. scutatum* kept in the laboratory. In both species the integrity of the shelter site is maintained and a territory thus defined. However, it should be noted that in nature the home ranges and territories of these species can be expected to vary greatly in size and shape according to the available food supply, population density, terrain, and so forth. The selective advantage afforded individuals possessing a sheltered territory is obvious, for animals deprived of such a retreat must sustain heavy predation. Furthermore there is some evidence that the proper feeding reactions of an individual

are dependent on its possession of a home range and associated shelter site. Much additional work is called for in the study of territorialism in the amphibians. It would be