pared with a living species of the same genus (*Globoquadrina dutertrei*) in Table 1. Substantial levels of the more thermally stable amino acids are still present in the Miocene specimens. If it is assumed that the total concentration of amino acids in the Recent *G. dutertrei* approximates the original value of the Miocene species, about 67 percent of the original total content has been preserved in *G. altispira* and 56 percent in *G. dehiscens* (*12*). The less thermally stable amino acids are either absent (Cys, Met, and Arg residues) or present at greatly reduced levels (Thr and Ser residues).

The second question, regarding the persistence of original specific differences, was approached by studying the same two species (*G. altispira* and *G. dehiscens*) since they are morphologically distinct. Because of the parallelism in Recent specimens, one would predict from the morphologies that the amino acid patterns should be generally similar but should differ significantly in the more sensitive (variable) amino acids (such as Asp and Gly residues). A plot of the two compositions (Fig. 2) confirms this prediction. Thus, diagenesis does not obliterate significant differences in original amino acid compositions (*13*).

Contamination is always a potential problem in interpreting low-level occurrences of amino acids in geologic environments (*6*). However, several lines of evidence developed during the study strongly argue against the presence of amino acids from sources other than calcified proteins (*5*).

As the amino acid composition of the test apparently reflects the genotype of both living and fossil planktonic Foraminifera, this quantitative taxonomic character provides a new approach to constructing a "natural" classification based on phylogeny. Evolutionary lineages can now be traced paleontologically by studying biochemical, as well as morphological, variations through geologic time. The technique may also be useful in differentiating between species, subspecies, and phenotypic variants at a given horizon in time.

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13. The lower limit in fossil age for applying this method has not been determined but is currently being investigated through the analysis of successively older samples in the sediment column.
14. We are deeply grateful to J. D. Hays for his interest, encouragement, and suggestions throughout this investigation. Special thanks are due S. S. Streeter for his valuable help in conducting and interpreting the factor analyses. Gratitude is expressed to A. W. H. Bé and T. Saito for their valuable advice on questions of foraminiferal taxonomy and evolution. We thank P. H. Abelson, A. W. H. Bé, W. S. Broecker, T. C. Hoering, and T. Saito for reviewing the manuscript and making many helpful suggestions. J. E. Damuth brought core V25-59 TW to our attention. D. Breger drafted the figures and D. Ultsch prepared the manuscript. The deep-sea cores were collected on cruises of the Lamont-Doherty Geological Observatory research vessel, supported by ONR grant N00014-67-A-0108-0004 and NSF grant GA-29460. Work done at Lamont-Doherty Geological Observatory was supported by ONR grant N00014-67-A-0108-004, NSF grant GA-29460, and a predoctoral fellowship from the Geophysical Laboratory, Carnegie Institution of Washington. Contribution No. 1796 of the Lamont-Doherty Geological Observatory.

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Chemical Methods for Removing Radon and Radon Daughters from Air

Abstract. *Liquid bromine trifluoride and the solid complexes* ClF_2SbF_6, BrF_2SbF_6, $BrF_4Sb_2F_{11}$, $IF_4(SbF_6)_3$, *and* BrF_2BiF_6 *react spontaneously with radon and radon daughters at 25°C, converting the radioelements to nonvolatile ions and compounds. The reagents can be used in gas-scrubbing units to remove radon and radon daughters from air. The halogen fluoride–antimony pentafluoride complexes may be suitable for purifying air in uranium mines and analyzing radon in air, since they have low dissociation pressures at 25°C and are less hazardous to handle than liquid halogen fluorides.*

The chief radiation hazard to miners in underground uranium mines is that from radon gas, released by the decay of radium, and the short-lived radon daughters (^{218}Po, ^{214}Pb, ^{214}Bi, and ^{214}Po). Medical and epidemiological studies have shown that prolonged exposure to high concentrations of these radioelements, particularly the radon daughters, increases the incidence of lung cancer among miners (*1*). Since the discovery of this hazard, uranium mines have been force-ventilated to reduce the concentrations of the radioelements. In the United States, federal regulations now require mine atmospheres to be controlled so that a miner receives no more than four "working level months" of radiation exposure in any 12-month period, the "working level" being defined as the concentration of short-lived radon daughters in

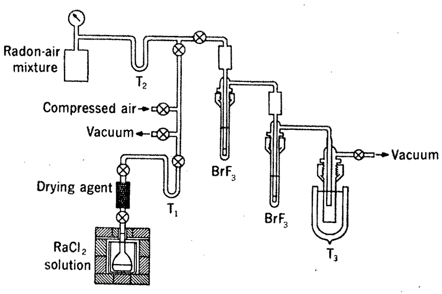

Fig. 1. Apparatus for testing the removal of radon from air with BrF_3.

equilibrium with 100 pc of radon-222 per liter of air (*2*).

Although radon is a noble gas, it is not completely inert but reacts with fluorine at 400°C to form a stable, ionic compound (*3*). Recently it has been shown that radon can be oxidized by halogen fluorides at 25°C and converted to a nonvolatile cation in several fluoride solvents (*4*). This finding has suggested the possibility of using chemical reagents to remove both radon and radon daughters from air. I report here some initial tests of laboratory-scale air purification units containing liquid BrF_3, solid complexes of halogen fluorides and metal fluorides, and simple metal fluorides.

The apparatus used in tests with liquid BrF_3 is shown in Fig. 1. For each test, ^{222}Rn was collected from a 30-mc $RaCl_2$ solution in a metal vacuum line, purified by low-temperature distillation from trap T_1 to trap T_2, and mixed with dry air. The mixture was then passed through two Kel-F test tubes in series, each containing 4.0 ml of BrF_3 at room temperature (23° to 25°C), and through trap T_3, which was cooled with liquid nitrogen. Any radon passing through the two-stage scrubber without reacting with the BrF_3 was expected to condense in T_3. To ensure good contact between gas and liquid, the gas was dispersed as very fine bubbles by a stainless steel frit in each tube. At the conclusion of the test, the position of radon was determined by measuring the γ emission of daughters ^{214}Pb and ^{214}Bi from each tube and from T_3. The measurements were repeated after several hours, when radon and the short-lived daughters were known to be in radioactive equilibrium.

In three experiments, mixtures of 3.1, 3.2, and 1.9 mc of radon and 0.69, 0.96, and 0.78 liters of air, respectively, were passed through the system at flow rates of 2.9 to 3.0 ml/min. Radon and radon daughters were found only in the first tube each time; no γ emission was detected from the second tube or T_3. All of the radioelements were therefore removed from the air stream with high efficiency in the first unit of the scrubber.

Bromine trifluoride is the most suitable halogen fluoride for use in units of this type at ambient temperatures, since it has a low vapor pressure (8 torr at 25°C). However, several more volatile halogen fluorides (ClF, ClF_3, ClF_5, BrF_5, and IF_7) also oxidize radon and might be used in similar air-purification units at lower temperatures.

Table 1. Removal of radon from air with solid fluorinating reagents. STP, standard temperature and pressure.

Compound	Amount of radon (mc)	Volume of air [liters (STP)]	Radon removed (%)
$KBrF_4$	2.8	0.76	28
$CsBrF_6$	2.2	.76	7
$KClF_4$	4.9	.69	19
$RbClF_4$	3.4	.69	16
ClF_2SbF_6	15.0	.69	100
BrF_2SbF_6	8.0	.69	100
$BrF_4Sb_2F_{11}$	3.7	.69	100
$IF_4(SbF_6)_3$	7.4	.69	100
IF_4SbF_6	3.6	.69	76
$NOSbF_6$	2.0	.69	0
BrF_2TaF_6	3.0	.69	27
BrF_2BiF_6	3.4	.69	100
AgF_2	1.5	.69	0
CoF_3	1.9	.69	0

For tests of solid fluorinating reagents, the tubes containing BrF_3 were replaced by a single Kel-F U-tube with an inner diameter of 6.3 mm. This was packed with a 50- to 100-mm-long section of powdered reagent. The same test procedure was used; a mixture of radon and air was passed through the powder at room temperature, then through trap T_3 at liquid nitrogen temperature, and the distribution of radon and radon daughters was determined from the γ emission.

Complex fluorides, such as $KBrF_4$, ClF_2SbF_6, and BrF_2TaF_6, were prepared for the tests by warming and shaking metal fluorides with halogen fluorides (10 to 20 percent excess) in nickel test tubes. The excess reagents were then pumped off, and the solids were powdered and loaded into U-tubes in a dry box. Complexes containing the cations ClF_2^+, BrF_2^+, BrF_4^+, IF_4^+, and IF_4^{3+} were prepared with Lewis acids (F^- acceptors SbF_5, TaF_5, and BiF_5), and complexes containing the anions ClF_4^-, BrF_4^-, and BrF_6^- were prepared with Lewis bases (F^- donors KF, RbF, and CsF). Many compounds of both types are known (*5*), and several have been used previously as fluorinating agents for metal oxides at high temperatures (*6*).

Table 1 shows the results obtained with the solid reagents at flow rates of 5.3 to 11.5 ml/min. Radon and radon daughters were removed from air most efficiently by halogen fluoride complexes of SbF_5 and BiF_5. The weaker complexes of TaF_5 and alkali metal fluorides removed only part of the radon, and AgF_2, CoF_3, and the nitrosyl complex $NOSbF_6$ (prepared from NOF and SbF_5) failed to react with radon. Since the nitrosyl complex contains SbF_6^- ion, it is clear that this ion is not an oxidant for radon in the similar halogen fluoride complexes ClF_2SbF_6, BrF_2SbF_6, IF_4SbF_6, and $IF_4(SbF_6)_3$; the cations are the oxidizing moieties. The iodine pentafluoride complex IF_4SbF_6 retained 76 percent of the radon in its test mixture, which is surprising, because neither IF_5 nor SbF_5 alone oxidizes radon (*4*). The IF_4^+ cation is therefore a stronger oxidizing agent than its parent, IF_5.

Radon is probably converted to a complex ion, RnF^+, in the reactions with the acid complexes as follows:

$$Rn + ClF_2^+SbF_6^- \rightarrow RnF^+SbF_6^- + ClF \quad (1)$$

$$Rn + BrF_2^+SbF_6^- \rightarrow RnF^+SbF_6^- + BrF \quad (2)$$

$$Rn + BrF_4^+Sb_2F_{11}^- \rightarrow RnF^+SbF_6^- + BrF_2^+SbF_6^- \quad (3)$$

$$Rn + IF_4^{3+}(SbF_6^-)_3 \rightarrow RnF^+SbF_6^- + IF_4^+Sb_2F_{11} \quad (4)$$

$$Rn + BrF_2^+BiF_6^- \rightarrow RnF^+BiF_6^- + BrF \quad (5)$$

Krypton and xenon are not oxidized by the solid reagents at 25°C, but KrF_2 and XeF_2 form adducts with SbF_5 (*7*) which are very similar to $RnF^+SbF_6^-$. Spectral studies (*8*) have shown that the xenon compound is ionic, with the formula $XeF^+Sb_2F_{11}^-$.

The halogen fluoride–antimony pentafluoride compounds appear most promising for use in uranium mines, since they remove radon and radon daughters from air efficiently and are less hazardous to handle than liquid halogen fluorides (*9*). Although sensitive to moisture, they are stable in dry air and can be stored indefinitely in metal and fluorinated plastic containers. Vapor emissions from the compounds also are very low. The dissociation pressure of BrF_2SbF_6 is less than 0.01 torr at 25°C (*6*), and the dissociation pressures of the other compounds probably are below 5 torr at 25°C.

At present, only radon daughters are removed from secondary (recirculated) air in uranium mines with fiber filters. Radon passes through the filters and continuously generates new daughters. By capturing the radon as well as the daughters in a chemical scrubber, this cycle could be ended and the total concentration of radioelements in the air could probably be greatly reduced.

Mine air is usually very humid, and the air would have to be dried before passage through a radon scrubber because water vapor decomposes the fluorinating chemicals. Industrial air-drying units containing silica gel desiccant or moisture-condensing coils might be used for this purpose. A complete air-purification system for a very active mine area, such as a working stope, might consist of the following components (in series): (i) an air-drying unit; (ii) a fluorinating unit; (iii) a halogen vapor-trapping unit (containing soda lime or activated alumina); and (iv) a blower for circulating the air through the three units and the external area. Only the air passing through the purification system would be dried, and, if necessary, it could be rehumidified for the comfort of the miners.

The lifetime of a bed of fluorinating chemical in a system of this type would depend on the water content of the air after drying, since the radon content of air is completely negligible in a chemical sense. A radon concentration of 100 pc/liter corresponds to only 6.5×10^{-16} g/liter, for example; this can be compared with 0.0114 g/liter of water vapor in air with a relative humidity at 25°C of 50 percent and 8.0×10^{-7} g/liter in extremely dry air with 1 part per million of residual water vapor (by volume). It is apparent from these numbers that the bed would be depleted by reaction with water vapor rather than by reaction with radon.

Several physical methods have been used for the collection of radon for analysis, including low-temperature condensation of the element (*10*) and adsorption of the element on activated charcoal and silica gel at −80°C (*11*). Both the physical and the chemical methods warrant further study for the decontamination of mine air. Some of the same problems are encountered with both physical and chemical methods. Water vapor and carbon dioxide saturate charcoal and silica gel, for example, and must be removed before radon can be adsorbed on these materials.

The halogen fluoride–antimony pentafluoride compounds probably can be used for the analysis of radon in air. Preliminary tests have shown that 5 pc of ^{222}Rn can be detected in a cartridge device with standard γ-counting equipment after equilibrium between radon and radon daughters has been established (*12*). Since the air in a uranium mine may contain 30 pc or more of ^{222}Rn per liter, a relatively small volume of air should provide an adequate sample for analysis.

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13. I thank H. H. Hyman for advice and helpful discussions, I. Ahmad for analyses of γ-ray spectra, C. Williams for technical assistance, and T. Surles for samples of $CsBrF_6$ and $RbBrF_4$. Work was performed under the auspices of the U.S. Atomic Energy Commission.

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High-Temperature Superconductors, the First Ternary System

Abstract. *A new system of high-temperature superconductors is reported. The compounds,* $Mo_{6-x}A_xS_6$ *where A is Cu, Zn, Mg, Ag, Cd, Sn, or Pb, are rhombohedral with* $a \simeq 6.5$ *angstroms and* $\alpha \sim 90°$. *The transition temperatures range from* ∼ *2.5°K for the Cd compound to* ∼ *13°K for the Pb compound.*

During the last few years a number of new superconductors have been discovered among the transition metal chalcogenides. Most of these are layer compounds in which the sequence of layers is -S-S-M-S-S-M-, where M is a transition metal. The metal-to-metal interactions between layers are weak and the compounds have a pseudo two-dimensional network of metal atoms. It is possible to intercalate these compounds with, for example, alkali metals, and in this case the highest reported superconducting transition temperature is ∼4.5°K for K_xMoS_2 (*1*). However, where a structure containing a true three-dimensional network of metal atoms is synthesized from similar elements, the transition temperatures are much higher, for example, ∼ 13°K for $Li_{0.3}Ti_{1.1}S_2$ (*2*).

In our search for new chalcogenides with a three-dimensional network of metal atoms, we found an entirely new system of high-temperature superconductors: $Mo_{6-x}A_xS_6$, where A is Cu, Mg, Zn, Cd, Ag, Sn, or Pb. These compounds were first synthesized by Chevrel *et al.* who mixed the elements or the sulfides in quartz ampoules at

Table 1. Superconductivity of ternary molybdenum sulfides.

Composition	Superconducting transition temperature (°K)	Lattice constants * (Å)			
		Rhombohedral axes		Hexagonal axes	
		a	*α*	*a*	*c*
$Mo_{4.5}Cu_{1.5}S_6$	10.9–10.8	6.51	95°18′	9.63	10.18
Mo_5ZnS_6	3.0– 2.7	6.489	94°41′	9.545	10.282
$Mo_{4.8}Ag_{1.2}S_6$	8.9– 8.4	6.48	91°57′	9.32	10.83
Mo_5CdS_6	2.4– 2.3	6.517	92°49′	9.440	10.720
$Mo_{5.1}Mg_{0.9}S_6$	2.5– 2.4	6.510	93°35′	9.490	10.550
Mo_5SnS_6	11.3–10.9	6.52	89°44′	9.19	11.34
$Mo_{5.1}Pb_{0.9}S_6$	13.2–12.5	6.54	89°28′	9.20	11.43

* The lattice constants for the Cu compounds are from this report. All the others are from (*3*).