fidently referred to *Palaeeudyptes antarcticus.* Brodkorb (6) placed the two Burnside specimens in a distinct species, *Palaeeudyptes marplesi,* which is probably valid for the holotype. The other Burnside and Concord specimens cannot be clearly identified to species on present evidence.

The Burnside mudstone is in part Kaiatan and in part Runangan (7), and the penguins from it may be of either age. The Concord greensand is Waitakian, but its microfauna is in part redeposited from the Burnside mudstone (7), and there is a strong possibility that its penguins are also derived from the older formation. Thus the specimens from the two formations in this quarry probably do not represent a single species, probably did not live over the long Kaiatan-Waitakian span, and may well all be of nearly or even precisely the same age.

The holotype of the first fossil penguin ever described, *Palaeeudyptes antarcticus* Huxley, 1859, came from the vicinity of Kakanui and has been generally considered Whaingaroan, early Oligocene, in age, as probably derived from the formation now called McDonald limestone (8). Such origin does not exclude the possibility of its being of Duntroonian, middle or late Oligocene age. From the scanty original data it seems at least equally probable that the specimen was in what is now called the Otekaike limestone, typical Waitakian, late Oligocene or early Miocene. It is also possible, but apparently less probable, that it was in the Totara limestone, Runangan, late Eocene. At present no specimens other than the holotype can be certainly referred to this species.

Platydyptes novaezealandiae (Oliver, 1930), considered to be probably Waitakian (5), late Oligocene or early Miocene, could as well be Duntroonian, middle or late Oligocene. *Platydyptes amiesi* Marples, 1952, and *Korora oliveri* Marples, 1952, were described as from the Waitakian, late Oligocene or early Miocene, without explicit evidence as to age (5). The age assignment is acceptable on Marples' authority. The usual assignment of *Pachydyptes ponderosus* Oliver, 1930, to the Runangan, latest Eocene, is almost certainly correct. Nor is there any doubt that *Archaeospheniscus lowei* Marples, 1952, *A. lopdelli* Marples, 1952, and *Duntroonornis parvus* Marples, 1952, are Duntroonian, middle or late Oligocene in age.

These changes in the dating of New Zealand forms considerably dilute the data hitherto used in reference to penguin distribution [for example, (9)]. However, they do not introduce any positive evidence against Stonehouse's conclusions.

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Ionic Radon Solutions

Abstract. *Radon is oxidized between −195° and 25°C by chlorine fluorides, bromine fluorides, iodine heptafluoride, and* NiF_6^{2-} *ion in hydrogen fluoride with the formation of stable solutions of radon fluoride. Electromigration studies show that the radon is present as a cation, possibly* Rn^{2+} *or* RnF^+, *in several conducting solutions.*

Radon fluoride does not closely resemble krypton or xenon fluorides, which are volatile at room temperature and dissolve in many solvents as molecular species. Weinstock (1) suggested that ionic bonds might be present in the radon compounds, in contrast to covalent bonds in the krypton and xenon compounds, since radon fluoride is involatile in vacuum below 200°C and the first ionization potential of radon (10.75 volts) is lower than that of krypton (14.00 volts) or xenon (12.13 volts). Solutions of radon fluoride in chlorine trifluoride, bromine trifluoride, and bromine pentafluoride solvents have been prepared (2); these offer new possibilities for exploring the chemistry of radon and differentiating between bond types. Some further studies of the oxidation of the element by halogen fluorides and metal fluorides are described in this report. Electromigration experiments are also described, which show that oxidized radon is a cation in several of the fluoride solutions.

Table 1. Free energies of reduction of some halogen and metal fluorides.

Reaction	ΔG°_{298} (kcal/mole)	References
$ClF_5(l) \rightarrow ClF_3(l) + F_2(g)$	6.0	(8)
$2ClF(l) \rightarrow Cl_2(g) + F_2(g)$	13.6	(8)
$IF_7(l) \rightarrow IF_5(l) + F_2(g)$	13.7	(9, 10)
$ClF_3(l) \rightarrow ClF(l) + F_2(g)$	21.4	(8)
$BrF_5(l) \rightarrow BrF_3(l) + F_2(g)$	27.0	(8)
$2BrF(g) \rightarrow Br_2(l) + F_2(g)$	35.3	(8, 9)
$BrF_3(l) \rightarrow BrF(g) + F_2(g)$	39.9	(8, 9)
$AsF_5(l) \rightarrow AsF_3(l) + F_2(g)$	61.2	(11, 12)
$IF_5(l) \rightarrow IF_3(g) + F_2(g)$	(79)*	(9, 10)
$SbF_5(l) \rightarrow SbF_3(s) + F_2(g)$	(90)*	(13)

* Estimated value.

Samples of gaseous ^{222}Rn (0.5 to 28 mc) were collected from a 30-mc radium chloride solution in a metal vacuum line, dried over calcium sulfate, and condensed in a cold trap at −195°C. After radiolytic hydrogen and oxygen were pumped off, the samples were distilled at −78°C into Kel-F test tubes that contained 0.5 to 3.0 ml of the following purified reagents frozen at −195°C: ClF, ClF_3, ClF_5, BrF_3, BrF_5, IF_5, IF_7, HF, AsF_5, and SbF_5; equimolar Br_2 and BrF_3; 5 mole percent BrF_3 in HF, BrF_5 in HF, and BrF_3 in IF_5; 0.1 mole percent K_2NiF_6 in HF. The mixtures were melted and then stirred with a Vortex stirrer. Solutions with very high vapor pressures (ClF, ClF_5, and AsF_5) were kept cold with refrigerant baths, whereas the others were allowed to warm to room temperature. After 1½ hours, the solutions were vacuum distilled to approximately one-third of their original volumes or to dryness. Distillate fractions and residues were allowed to stand for 3 hours to permit radon daughters (^{214}Pb and ^{214}Bi) to reach equilibrium again, then total gamma activity was determined. The radon remained behind as involatile radon fluoride in all of the solutions except IF_5, HF, AsF_5, and SbF_5. In the latter solutions, the radon was not oxidized and appeared in the first distillate fractions.

The composition of the radon fluoride has not yet been determined, since only very small amounts of solid have been obtained by evaporating the solutions to dryness [0.2 μg or less in these experiments and 2.0 μg or less

Table 2. Electromigration of radon in fluoride solutions: A, BrF_3; B, 5 mole percent BrF_3 in HF; C, 5 mole percent BrF_3 in IF_5; D, 5 mole percent BrF_3 in IF_5, saturated with CsF; E, 5 mole percent BrF_5 in HF, saturated with KF.

Solution	Radon added (mc)	Potential difference (volts)	Current (ma)	Radon concentration after 1 hour of electrolysis (mc/ml)		
				Cathode solution	Center solution	Anode solution
A	5.6	32	50	0.31	0.68	0.00
B	17.5	50	20	0.87	1.18	0.02
C	4.6	50	<2	0.00	1.55	0.00
D	23.2	50	15	1.49	2.16	0.19
E	19.5	18	50	0.98	1.11	0.11

in previous experiments (*2*)]. Residues from chlorine trifluoride and bromine trifluoride solutions have been examined with a mass spectrometer (Bendix Time-of-Flight) (*3*), but no mass peaks of radon compounds have been observed at room temperature, and only decomposition products (radon, fluorine, and impurities) have been observed above 250°C. The residues liberate radon quantitatively when hydrolyzed with water, dilute alkalis, or dilute acids, which suggests that radon is present as the difluoride, since krypton difluoride and xenon difluoride hydrolyze in the same manner:

$$KrF_2 + H_2O \rightarrow Kr + \tfrac{1}{2}O_2 + 2\ HF$$

$$XeF_2 + H_2O \rightarrow Xe + \tfrac{1}{2}O_2 + 2\ HF$$

$$RnF_2 + H_2O \rightarrow Rn + \tfrac{1}{2}O_2 + 2\ HF$$

Thus far no oxygenated radon species analogous to XeO_3 or $XeO_6{}^{4-}$ have been detected in the aqueous solutions. The oxygenated xenon species are formed very readily when xenon tetrafluoride and xenon hexafluoride are hydrolyzed (*4*).

Molar free energies of reduction of all of the fluoride reagents except K_2NiF_6 are listed in Table 1. The order is that of increasing stability of the compounds (increasing positive $\Delta G°$ for reduction to a lower fluoride and fluorine). Bromine trifluoride and all the preceding compounds in the series oxidize radon, whereas arsenic pentafluoride and compounds lower in the series do not react with radon. The free energy of formation of radon fluoride (in solution, per mole of diatomic fluorine required) must therefore lie between the free energies of reduction of bromine trifluoride and arsenic pentafluoride. If radon is introduced into the liquids at a concentration of 10.0 mc/ml (2.93×10^{-7} mole/liter) and products are formed at the same concentration, the free energy correction from actual states to standard states is approximately 10.5 kcal/mole. The standard free energy of formation must then lie between the limits of —29 and —51 kcal/mole. These limits are, indeed, very far apart, but can probably be narrowed by further experiments with fluorides intermediate in oxidizing power between bromine trifluoride and arsenic pentafluoride.

The reactions of radon which are thermodynamically possible occur spontaneously, even at low temperatures, when 1 mc (or more) of the element is confined in a small volume (100 ml or less) with oxidizing agents. Photochemical or thermal activation is unnecessary, since large numbers of ions and excited atoms are produced by the alpha particles from radon and its daughters. This self-activation is not surprising, since radon alphas have been used to initiate reactions in many chemical systems [combination of hydrogen and oxygen, for example; combination of nitrogen and oxygen; decomposition of ammonia; polymerization of acetylene, ethylene, and cyanogen (*5*)].

The electromigration of oxidized radon was studied in the cell shown in Fig. 1. The d–c voltage was supplied by a rectifier unit. The cell was filled with 20 ml of inactive solution, such as BrF_3 or $HF\text{-}BrF_3$, in each experiment, and radon in 1.0 or 2.0 ml of the same solvent was added to the center leg without stirring. The solution was then electrolyzed for 1 hour at 18 to 50 volts. At the end of this period, 1.0 ml samples of liquid were removed from the three legs, transferred to Kel-F test tubes, and counted for total gamma activity at 2-hour intervals. Solutions containing hydrogen fluoride were electrolyzed at 0°C, due to the high vapor pressures, whereas the others were electrolyzed at room temperature (*6*) (Table 2).

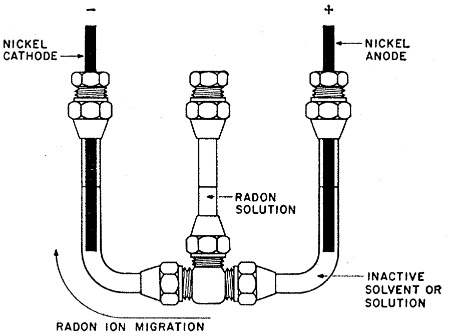

Fig. 1. Kel-F electrolysis cell, with brass flare connectors and nickel electrodes (6.3 mm diameter and 15 cm apart).

Radon migrated only to the cathode in pure bromine trifluoride, which is an ionizing solvent with moderately high conductivity. The radon was not discharged as gas but remained in the cathode liquid, as very little alpha activity was detected with a survey meter in the air above the loosened cathode plug. The current was carried chiefly by $BrF_2{}^+$ and $BrF_4{}^-$ ions in this system, rather than by radon ions, and BrF and BrF_5 were produced at the cathode and anode, respectively.

Radon also migrated to the cathode in a solution of 5 mole percent BrF_3 in HF. A small amount of radon was found in the anode liquid in this instance, possibly due to diffusion or mixing, because the cell was not divided into compartments by porous barriers. Gas was evolved at the cathode during the electrolysis (probably hydrogen), but the count of alpha particles above the cell remained low.

No radon was detected in the cathode or anode liquid of a solution of 5 mole percent BrF_3 in IF_5 after electrolysis, as this was a poor electrical conductor. In solutions of $BrF_3\text{-}IF_5$ saturated with cesium fluoride and $BrF_5\text{-}HF$ saturated with potassium fluoride, migration to the cathode occurred, as before. Anionic radon species may have been present in the latter solutions as well as cationic species, because appreciable concentrations of radon were found in the anode liquids. The cations RnF^+ and Rn^{2+} would be expected to be formed by the dissociation of radon difluoride, but in solutions containing high concentrations of fluoride ion, dissociation would be suppressed and anionic species might also be formed.

There is a remarkable similarity in the behavior of astatine and radon in fluorination experiments. The two elements lie in adjoining columns of the periodic table, and both would be expected to form volatile fluorides by extrapolation from fluorides of preceding elements (that is, from ClF, BrF, and IF in the one instance and KrF_2 and XeF_2 in the other instance). However, astatine and radon follow the long rare earth series of elements and are probably more "metallic" than anticipated. Appelman *et al.* (*7*) observed the volatile halides AtI, AtBr, and AtCl in mass spectrometric experiments but were unable to observe the corresponding fluoride after treating astatine with chlorine trifluoride. Probably an involatile ionic fluoride was formed, with properties similar to radon fluoride. (AtF would be isoelectronic with RnF^+, the complex ion postulated to be present in the radon solutions.)

Practical applications may be found for the new radon solutions in the preparation of radiation sources, collection of radon for analysis, and removal of radon from the air of uranium mines. For medical use, radon "seeds" or "needles" are prepared at the present time, as in the past, by sealing radon gas into gold capillary tubes. The solutions offer new possibilities for metering and handling radon conveniently in nonvolatile form. By evaporating the solutions to dryness from metal foils, porous materials, or plastics, and either coating or encapsulating the deposits to absorb alpha particles, gamma radiation sources can probably be made in a variety of new forms. The oxidizing solutions offer possibilities for collecting radon from large volumes of air in bubble trains or other gas-liquid contact devices. In uranium mines, high concentrations of radon constitute a major health hazard to miners who are exposed to the atmospheres for long periods of time. Forced ventilation is used to reduce the radon concentrations, but alternatively, chemical scrubbers can probably now be devised which will allow the air to be purified and recirculated.

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Pyroxferroite: Stability and X-ray Crystallography of Synthetic $Ca_{0.15}Fe_{0.85}SiO_3$ Pyroxenoid

Abstract. *Synthetic $Ca_{0.15}Fe_{0.85}SiO_3$ pyroxenoid has the same (pyroxmangite) structure and very nearly the same composition as pyroxferroite, a new mineral found in Apollo 11 lunar samples. The synthetic material is not stable below pressures of approximately 10 kilobars. It appears likely that the lunar pyroxferroite has persisted in a metastable state for some billions of years.*

An unidentified yellow mineral reported by the preliminary examination team (*1*) in lunar samples from Mare Tranquillitatis is a pyroxenoid with the pyroxmangite structure, but it contains very little Mn or Mg (*2–5*). This mineral, which has been named pyroxferroite (*6*), has not been found in terrestrial rocks. We report here data on the stability and crystallography of a synthetic pyroxenoid with the pyroxmangite structure and the composition $Ca_{0.15}Fe_{0.85}SiO_3$, which is very close to that reported for some of the lunar samples.

Ferrosilite III, one of the several polymorphs of pure $FeSiO_3$ synthesized at high pressures (*7*), was shown by Burnham (*8*) to be structurally related to the pyroxenoid minerals. Indications of triclinic diffraction symmetry, and one unit cell dimension of 22.61 Å, led Burnham to hypothesize that ferrosilite III represents an extension of previously known pyroxenoid structures to one with single silicate chains having a repeat length consisting of nine silica tetrahedra—a *Neunerkette* (*9*).

The synthesis and identification of ferrosilite III fitted well with Liebau's (*10*) suggestion that repeat lengths of silicate chains in pyroxenoids are at least partially controlled by average octahedral cation size. Pure wollastonite ($CaSiO_3$) is a pyroxenoid with a repeat length of three silica tetrahedra (a *Dreierkette*) (*11*). We anticipated that pyroxenoids containing intermediate amounts of Ca and Fe might have the *Fünferketten* structure, as found in rhodonite, and that, as the iron content increases and the average octahedral cation size decreases, the pyroxenoids might have the *Siebenerketten* pyroxmangite structure.

Bowen *et al.* (*12*) synthesized pyroxenoids containing Ca and Fe ranging in composition from pure $CaSiO_3$ to approximately $Ca_{0.28}Fe_{0.72}SiO_3$ (mole ratio), but the fine grain size and limited x-ray equipment available to them precluded any identification more definite than "wollastonite solid solution." To our knowledge, no modern study has confirmed that their iron-rich pyroxenoids do in fact have the *Dreierketten* (wollastonite) structure. It was subsequently shown (*13*) that pyroxenoids more rich in iron than approximately $Ca_{0.37}Fe_{0.63}SiO_3$ are not stable at low pressures (below 2 kb), yet with increasing pressure pyroxenoids progressively more rich in iron become stable (*14*). By careful choice of pressure and temperature for each composition, we have succeeded in synthesizing a complete range of pyroxenoids from $Ca_{0.5}Fe_{0.5}SiO_3$ to $FeSiO_3$. We have found by single-crystal precession photography that a synthetic pyroxenoid of composition $Ca_{0.15}Fe_{0.85}SiO_3$ has the predicted *Siebenerketten* silicate chain configuration. Thus this phase is a manganese- and magnesium-free analog of pyroxmangite and has the same structure as well as very nearly the same composition as the lunar pyroxferroite (*2–5*).

We obtained single crystals from an experiment in which synthetic clinopyroxene of $Ca_{0.15}Fe_{0.85}SiO_3$ composition was inverted to pyroxenoid at 12.5 kb and 1175°C. Precession photographs showed patterns similar to those seen on photographs of ferrosilite III,