GEOLOGICAL SURVEY
TEPCO
RECEIVED

FEB 16 1955

Denver

Ops w.s.T.

Those below

February 11, 1955

J. H. Eric

Classification of TEI-11, The occurrence of xenon

It seems that at least some Survey copies of TEI-11 are, incorrectly, classified SECRET (defense information), whereas, AEC copies are, correctly, unclassified. When I called this to the attention of D. P. Kuntz, Division of Raw Materials, AEC, he suggested that we mark out the classification and the defense information marking on our copies, write "UNCLASSIFIED" on the covers of the reports and immediately below, "classified in error." Please do this if your copy is classified.

A. L. Brokaw
A. P. Butler, Jr.
F. J. Flanagan
V. E. McKelvey
C. F. Withington

TEPCO Library
RECEIVED
FEB 18 1955
U. S. GEOLOGICAL SURVEY
DENVER, COLO.

JHE

NOTED

FEB 16 1955
TEPCO

Butler

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

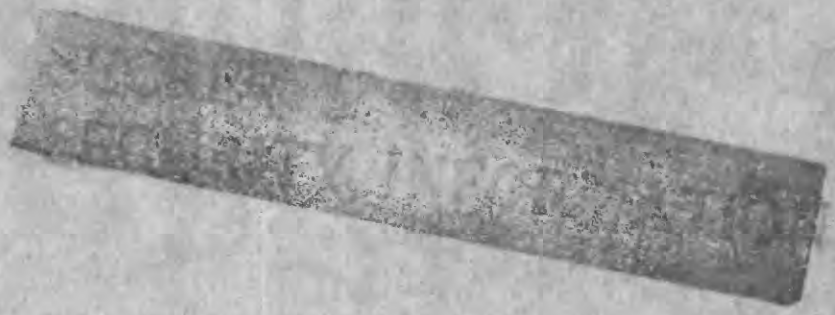
THE OCCURRENCE OF XENON

by

Michael Fleischer

May 1945

Trace Elements Investigations--Report No. 11



Contents

The Occurrence of Xenon

ABSTRACT

Xenon is one of the rarest of all the chemical elements. The only source at present is the atmosphere, from which it is recovered as a by-product, although the xenon content is only one pound in twelve hundred tons. Data on other possible sources are few, but no other source seems to offer much promise.

INTRODUCTION

This report on the occurrence of xenon is the second in a series of similar reports being prepared by the Geological Survey in response to an expression of interest in such information by a war agency.

Xenon is a chemical element having the atomic number 54 and the atomic weight 131.3. It belongs to the group of elements known as the inert gases and is characterized by its lack of reactivity. Only a few compounds, stable at low temperatures and high pressures, are known. A number of reviews of the element's history and properties are available (12, 23, 35, 36, 40).

GEOCHEMICAL CONSIDERATIONS

General statement

Xenon is one of the rarest of all the chemical elements. It was estimated recently (3) to form 3×10^{-9}% by weight of the earth's crust (including the atmosphere) and to be eighty-fifth in order of abundance of the ninety known elements.

The distribution of the xenon present in the earth has probably been modified by three main factors (15):

(1) Xenon is probably not uniformly distributed in the atmosphere, but should be concentrated by diffusion in the lowest layers. (2) Xenon is constantly being withdrawn from the atmosphere by solution in the waters of the earth. (3) As xenon is more soluble in water than the other inert gases, waters should be enriched in xenon relative to the other inert gases (except helium, which is being formed by radioactive disintegration). This last conclusion is verified by the recorded analyses.

The few analyses reported in the literature indicate that in natural gases, gases from waters, and volcanic gases, the relative amounts of the inert gases and of nitrogen are approximately the same as in air. That is, the ratios Xe/N, Xe/A, etc., are of the same order of magnitude as in air for most samples, although the absolute contents of xenon vary widely. A few samples have ratios Xe/N two to four, and exceptionally ten, times the ratio Xe/N in air. If this constancy of the ratio Xe/N shown by the available analyses is valid, there would be little prospect of finding gases with xenon contents significantly higher than that of the atmosphere.

Occurences

1. In the atmosphere

Two independent determinations (10, 29) of the xenon content of air gave 8×10^{-6} and 9×10^{-6} volume percent. This corresponds to 4×10^{-5} weight percent, or about one pound of xenon in twelve hundred tons.

2. In the gases of mineral springs

Analyses of the gases of mineral springs have been made chiefly by Moureu and Lepape, who have summarized their results (18, 25, 26, 27). Some analyses have been published by others (7, 30, 31). In all, approximately one hundred and fifty analyses of such gases have been published in the past fifty years,

but only twenty include determinations of xenon. Most have xenon contents less than that of air; a few have xenon contents two to five times that of air. Xenon is enriched relative to argon and the other inert gases, the average Xe/A ratio being approximately 1.8 times the Xe/A ratio in air. Assuming that this ratio is constant, one may calculate the xenon content of samples for which only argon determinations have been made. These estimated xenon contents are of the same order of magnitude as those actually determined.

3. In natural gases

Many analyses have been published of volcanic gases, gases from rocks, mine gases and natural gases (1, 16, 19, 27, 28, 32, 37, 38), but xenon has been determined in only sixteen, and argon in relatively few. The xenon contents reported have been much lower than that of air. The ratios Xe/A, A/N, etc., are more variable than in the gases from springs, but are within a power of ten of the ratios in air.

Data are entirely lacking for the inert gas content of the gases from which helium is being extracted in the United States. A few of these are rich in nitbgen, and these might be expected to have xenon contents approximating or slightly higher than that of air. The helium-rich gases that contain high percentages of hydrocarbons might be expected to contain less xenon than air.

RECOVERY OF XENON

In the fractional liquefaction of air, xenon is concentrated in the oxygen-rich fraction and is separated by a series of complex fractionation and adsorption processes. The recovery is stated to be about 75% (24). The processes used have been described by many authors (2, 5, 6, 7, 8, 9, 11, 13, 14, 17, 20, 21, 22, 24, 39). Increasing interest in the recovery of xenon (and krypton) is evidenced by the issuance in recent years of numerous patents on methods of recovery from air. Plants designed to recover only krypton and xenon from air have recently been put into operation (39).

The only other source of the inert gases that has been suggested is the waste gas from the synthesis of ammonia (14). This would probably be a possible source of argon, but nearly all the xenon should have been removed along with the oxygen.

POSSIBLE SOURCES OF XENON

The difficulty of separating xenon from other gases and the elaborate equipment required appear to exclude the possibility of its recovery from sources other than those, such as air, yielding other valuable constituents. On the basis of the few available data, there seems little likelihood that sources will be found with sufficiently high xenon contents to justify recovery of xenon alone.

SUGGESTIONS FOR FURTHER WORK

No information is available to the Geological Survey on the present production of xenon. Installation of recovery systems in plants not now recovering xenon appears to be the best available method of increasing the production.

It would also be desirable to have analyses made of samples of the gases from which helium is now being recovered, since these gases are being processed.

BIBLIOGRAPHY

Note: The original papers were seen except those for which reference to an abstract journal is given.

1. Allen, E. T. Chemical aspects of volcanism with a collection of the analyses of volcanic gases.
J. Franklin Inst. 193, 29-80 (1922).

None of the analyses give xenon; the few for which argon contents were determined give A/N ratios not much different than in air.

2. Allen, F. J. and Moore, R. B. Extraction of krypton and xenon from liquid air residues.
J. Am. Chem. Soc. 53, 2512-2522 (1931).

Laboratory-scale extraction is described, with a historical summary and bibliography.

3. Anderson, J. S. Chemistry of the earth.
J. Proc. Roy. Soc. New South Wales 76, 329-345 (1943).

A general account. Xenon is estimated to form $\sim 3 \times 10^{-9}$% by weight of the earth's crust and is the eighty-fifth in abundance of the ninety elements.

4. Aston, F. W. The rarity of the inert gases on the earth.
Nature 114, 786 (1924).

A plot of the abundance of atoms vs. their mass numbers shows that the inert gases are much rarer than would be expected, about one-millionth part of their proper quota. The remainder probably has been lost to the sun.

5. Boyer, Jacques. Industrial production of krypton (in French).
La Nature No. 2991, 558-561 (1936); Abstr. 31, 8128 (1937).

Description of the recovery of krypton and xenon from liquid air. One factory in France is said to produce thirty liters of krypton and four liters of xenon a day.

6. Claude, Georges. The industrial production of krypton and xenon. (in French).
Proc. Seventh Intern. Congr. Refrig. 1936, 1, No. 43, 379-381 (1937); Chem. Abstr. 32, 8219 (1938).

7. Claude, Georges. Sur l'extraction du krypton et du xénon de l'air et des gaz dissous dans l'eau.
Compt. Rend. 187, 581-585 (1928).

A description of the industrial extraction. Gases from natural waters have higher Xe/N and Xe/A ratios than air because the solubility of xenon in water is greater than those of the other inert gases.

8. Claude, Georges. The industrial extraction of krypton and xenon from the air, and a historical review of the industry engaged in the production of liquid air. Ice and Cold Storage 42, No. 497, 118 (1939); Rev. gén. froid 20, 223-229 (1939); Chem. Abstr. 34, 227, 7550 (1940).

9. Colton, H. S. Inert gases - their production and uses. Chem. Met. Eng. 44, 484-486 (1937).

A brief summary. It is stated that xenon costs $425,000 per cubic foot.

10. Damköhler, Gerhard. Neubestimmung des Krypton-und Xenon-Gehaltes der atmosphärischen Luft. Z. Elektrochem. 41, 74-80 (1935).

The average of six determinations was 0.08 volumes of xenon per million volumes of air = 8×10^{-6} volume percent.

11. Fastovsky, V. G. Separation of krypton and xenon. J. Applied Chem. U.S.S.R. 12, 675-684 (in Russian), 685 (in French) (1939).

A review.

12. Gross, P. P., Jr. Rare gases in everyday use. J. Chem. Ed. 18, 533-539 (1941).

A general account, including discussion of possible uses.

13. Jordan, R. B. Production of oxygen, nitrogen and rare-gas elements. Proc.-World Eng. Cong. Tokyo 1929, 31, 131-138 (1931); Chem. Abstr. 25, 5253 (1931

14. Kapustin, N. P. Rare gases in the wastes from the synthesis of ammonia. (in Russian). J. Chem. Ind. (U.S.S.R.) 13, 464-466 (1936); Chem. Abstr. 30, 5001 (1936).

Discussion of the enrichment of argon (and presumably krypton and xenon) in these wastes and the possibility of recovery.

15. Khlopin, V. G. Geochemistry of the noble gases. (in Russian). Compt. rend. acad. sci. U.R.S.S. 1931A, No. 11, 296-303. (From a translation by Taisia Stadnichenko.

The uniform distribution of the heavy rare gases is probably modified by two factors. Xenon should be concentrated somewhat by diffusion in the lower part of the atmosphere, but is also withdrawn from the atmosphere because of its solubility in water, higher than those of the other inert gases. The gases of waters

should therefore be relatively enriched in xenon, and this has been verified by experimental determinations.

16. Krejci-Graf, Karl. Zur Geochemie der Naturgase.
Kali 28, 249-252, 261-265, 275-278, 287-290 (1934).

Analyses of 108 natural gases, only a few of which include determinations of total rare gases.

17. Leclerc, Edm. and Haux, R. Les gaz rares, production et applications.
Rev. universelle mines 13, 350-354 (1937).
brief
A/review of recovery from air.

18. Lepape, Adolphe. Les gaz rares des eaux minérales.
Rev. quim. pura applicada 9, 29-46 (1934).

A review, listing analyses of gases from about fifty mineral springs. The amounts of the rare gases vary widely, but the ratios Xe/A, Xe/Kr, etc., do not vary much from the ratios in air.

19. Levi, M. G., Nasini, A. G. and de Cori, P. Gas rari e radioattività nei gas naturali idrocarburati italiani.
Gazz. chim. Ital. 62, 799-821 (1932).

Analyses are given of twenty-three hydrocarbon gases. Xenon was not determined. The ratio A/N was one to two times that in air.

20. Mathias, E. The industry of very low temperatures and of the rare gases.
Bull. Interm. Inst. Refrig. 15, 91-108A (1934); Chem. Abstr. 29, 4215 (1935).

A review.

21. Mathias, E. The rare gases.
Refrigerating Eng. 30, 196-198 (1935).

A review of the industry and new applications.

22. Mathias, E. The industry of very low temperatures and of the rare gases.
Bull. Intern. Inst. Refrig. 17, No. 4, A25-49 (1936); Chem. Abstr. 31, 5622 (1937).

A review.

23. Mellor, J. W. A comprehensive treatise on inorganic and theoretical chemistry.
Vol. VII. Longmans, Green and Co. (1927).

Pages 889 to 951 deal with the inert gases.

24. Metzger, F. J. Traces (of rare gases) from tons.
Ind. Eng. Chem. 27, 112-116 (1935).

A brief description of the recovery of xenon from air. It is stated that the recovery is about 75%.

25. Moureu, Charles. Recherches sur les gaz rares des sources thermales.
Bull. soc. chim. [4] 9-10, 1-25 (1911).

A review, with fifty-seven analyses of gases from thermal springs. No data are given on xenon content, only the total of argon + xenon + krypton was determined. A few contain more argon than air and the maximum recorded is 1.6 times that of air.

26. Moureu, Charles. Recherches sur les gaz rares des sources thermales; leur enseignements concernant la radioactivité et la physique du globe.
J. chim. phys. 11, 63-153 (1913).

A review, much as (25) above, but more detailed and with thirteen additional analyses.

27. Moureu, Charles. Les gaz rares des gaz naturels.
J. Chem. Soc. (London) 123, 1905-1947 (1923).

A review, see (25) and (26). Analyses are given of gases from 108 thermal springs with xenon determinations on 17. The ratio Xe/A varies from 1.2 to 2.5 times that of air. Six analyses of mine gases show very little argon and other rare gases.

28. Moureu, Charles and Lepape, Adolphe. Les gaz rares de grisous.
Ann. chim. 4, 137-157 (1915); 5, 5-51, 225-257 (1916).

A review. Five analyses of gases from coal mines show maximum content of argon + krypton + xenon of 0.04% by volume. The ratio Xe/A is approximately the same as in air.

29. Moureu, Charles and Lepape, Adolphe. Titre de l'air atmosphérique en krypton et en xénon.
Compt. Rend. 183, 171-175 (1926).

Air contains 0.000009% Xe by volume, 0.00004% by weight.

30. Nasini, A. G. Rapport sur les gaz rares des eaux minérales.
Rev. quim. pura applicada 8, 31-62 (1933).

Analyses are given of gases from 28 sources. No determinations of xenon are given, only determinations of argon + krypton + xenon. The ratio A/N is near that of air for most samples.

31. Pentchev, N. P. Sur la teneur en krypton et en xénon de quelques gas naturels de Bulgarie.
Compt. rend. 192, 691-693 (1931).

Analysis of gases from three springs gave 1 to 2 x 10^{-5}% Xe. The ratio Xe/A was nearly that of air.

32. Pietti, Arnaldo and Boggio-Lera, E. Sui gas nobili della esalazioni vulcaniche.
Rend. accad. sci. Napoli 30, 92-99 (1924).

Analyses are given of six volcanic gases for argon + krypton + xenon. The ratio A/N was slightly lower than in air for five gases, much lower in one.

33. Rabinowitsch, Eugen. Ueber den Gehalt der Luft an Krypton und Xenon.
Z. angew. Chem. 39, 737-738 (1926).

A review of determinations of the xenon content of air.

34. Ramsay, William. An attempt to estimate the relative amounts of krypton and xenon in atmospheric air.
Proc. Roy. Soc. London 71, 421-427 (1903).

An early determination, now superseded, see (10) and (29).

35. Ramsay, William. The gases of the atmosphere. Fourth Edition, 1915.

A general account.

36. Rutherford, Ernest. The rare gases of the atmosphere.
Engineering 121, 353-354, 388-390, 438, 458-459 (1926).

A brief review.

37. Sborgi, Umberto. Presenza del cripto e dello xeno, oltre che degli altri gas nobili, nei Soffioni boraciferi toscani. Aspetto geochimica della composizione nei Soffioni.
Mem. accad. Italia, Classe sci. fis. mat. nat. 8, 533-538 (1937).

Analyses of gases from ten fumaroles in Tuscany show 1.4 to 6.7 x 10^{-7}% by volume Xe or 0.0016-0.0074 times the content in air!

38. Shepherd, E. S. The gases in rocks and some related problems.
Am. J. Sci. 35A, 311-351 (1938).

Analyses are given of the gases removed from rocks. All are low in argon.

39. Siedler, Ph. The manufacture and utilization of the rare gases. (in German).
Angew. Chem. 51, 799-808 (1938).

A review, including descriptions of plants in France and Germany designed to recover only krypton and xenon from air.

40. Travers, M. K. The discovery of the rare gases. 128 pages. Edward Arnold and Co., London (1928).