Argon Isotopes in Natural Gases.

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Summary. - The Argon isotopic composition has been measured in many italian fumeroles and soffioni. A remarkable enrichment of A^{40} has been found, certainly due to the K^{40} decay in the inner of the earth. With the help of these data, the problem of the origin of atmospheric Argon is considered.

Introduction.

Natural gases have been studied for a long while to get informations on the inner of the earth. Chemical analyses of natural gases (volcanic gases, fumeroles, drill-hole gases and so on) have been made by many authors [1], but as far as we know the isotopic composition has not yet been considered.

Rare gases are always present in some amount in natural gases. Attention must be stressed to rare gases as invaluable sources of information on constitution, origin and evolution of the earth atmosphere.

Argon [2] isotopes are very interesting in this respect. The K^{40} disintegration was postulated by VON WEIZSÄCKER [3] to explain the great amount

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[1] For a review of these data see: U. SBORGI: *Ann. di Chim. Appl.*, **32**, 395 (1942).

[2] The Argon content in the atmosphere is 0,93% in volume. Its isotopic composition, as given by A. O. NIER: *Phys. Rev.*, **77**, 789 (1950), is

$$A^{36} \qquad 0.337 \pm 0.001 \%$$
$$A^{38} \qquad 0.063 \pm 0.001 \%$$
$$A^{40} \qquad 99.600 \pm 0.001 \%$$

[3] C. F. VON WEIZSÄCKER: *Phys. Zeits.*, **38**, 623 (1937).

of A⁴⁰ in the atmosphere. As a matter of fact K⁴⁰ (which is contained in natural Potassium as 0.0119 %) has been shown later to decay not only by β^- disintegration, but also ([4]) by K-capture, the final product of this second process being just A⁴⁰. Furthermore Potassium content in the earth has been shown ([5]) to be in such a large amount to justify the A⁴⁰ content in the atmosphere.

A question still open is the mechanism by which A⁴⁰ accumulated in the atmosphere ([6]). There is still some doubt whether a great amount of the actual A⁴⁰ was already contained in the primitive atmosphere, or whether it was continuously evolving in the geological time. In this respect the A⁴⁰/A³⁶ ratio in natural gases is a source of information for the A⁴⁰ amount which continually goes in the atmosphere.

Experimental part.

We starked our work in volcanic gases. It is a difficult task to capture true volcanic gases avoiding air contamination. A few attempts have been made to catch gases from Etna, Stromboli and Vulcano, introducing a vacuum tight tank as deep as possible in the vulcano gaps. A device was used to open and to close the tank right inside the gap, in order to prevent any air contamination. In all collected samples the enrichment factor

$$\eta = [\mathrm{A}^{40}/\mathrm{A}^{36}]_{\mathrm{gas}}/[\mathrm{A}^{40}/\mathrm{A}^{36}]_{\mathrm{atmophere}} ,$$

was so close to one to believe the collected smokes were not really coming from the inside of the volcano, but probably were some circulating air in the gaps.

For this reason we left volcanic gases for fumeroles and drill holes where the capture is much easier and safer (expecially for the experimentalist). As two samples provided by the interest of the Larderello Corporation were found ([7]) to have a η value larger than one, we collected further samples from the most important italian fumeroles and «soffioni» ([8]).

([4]) F. C. THOMPSON and S. ROWLANDS: *Nature*, **152**, 103 (1943).

([5]) H. E. TATEL: *Journ. Geoph. Res.*, **55**, 329 (1950); F. BIRCH: *Journ. Geoph. Res.* **56**, 107 (1951).

([6]) J. H. J. POOLE, C. F. G. DELANEY: *Nature*, **167**, 680 (1951); A. ROSTAGNI: *Geof. pura e applicata*, **18**, 128 (1950).

([7]) G. BOATO, G. CARERI, G. NENCINI and M. SANTANGELO: *Ann. di Geofisica*, **4**, 111 (1951).

([8]) «Soffioni» are high temperature and pressure steam wells, somewhat like geysers. Some of them carries to the atmosphere a hundred tons of water vapour per hour. For details see: P. GINORI CONTI: *Journ. Chem. Educ.*, **4**, 281 (1927); U. SBORGI: *Atti della Reale Acc. d'Italia*, **5**, 667 (1934).

« Soffioni » samples have been collected and purified by the Larderello Corporation. Fumerole gases have been collected by us with a bell immersed in the bubbling water. Water and carbon dioxide, the most abundant components ([9]), were both adsorbed on the spot. Rare gases were extracted in the laboratory in the usual way. A quantity of nearly 100 cm³ at 20 mmHg, suitable for isotopes analysis, was obtained working on one cubic meter of original gases at standard conditions.

A Nier-type mass spectrometer built in this laboratory ([10]) was used for isotopes analysis. For every sample the full mass spectrum in the range 35
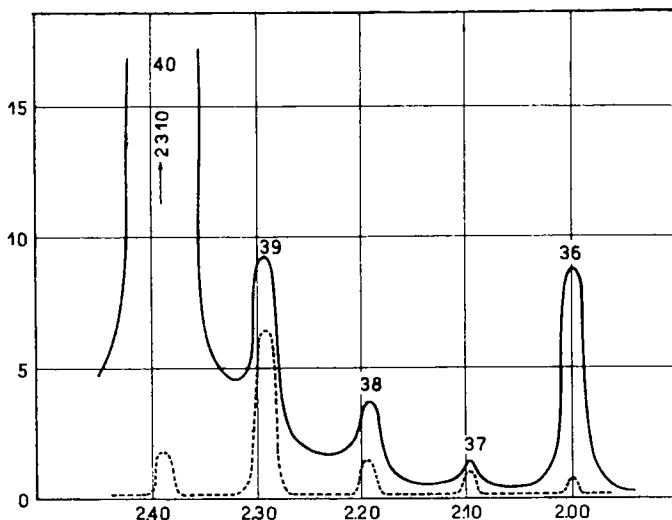

Fig. 1. -- The typical mass spectrum of atmospheric Argon, and the background (dotted curve) in the mass range 36 to 40. It is a plot of the ion current in arbitrary units versus the magnet current in Ampere.

to 41 has been measured and compared with an atmospheric Argon sample used as a standard. In this mass range the background had a constant value after the copper analyser tube had been heated at 200 °C for a few days. The background has been always measured before and after a sample has been introduced, and subtracted in the proper way. Due to the high in-

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([9]) Except for water, always present as vapour or also in condensed form, carbon dioxyde constitutes 90-99% of these gases. No appreciable oxygen quantities are generally found, instead Nitrogen and rare gases are always present. Other gases, like Hydrogen, Hydrogen sulfide, Methane, are sometimes present in small amount as reported in reference ([1]).

([10]) G. CARERI and G. NENCINI: *Nuovo Cimento*, **7**, 64 (1950).

tensity of mass 38 background peak, the Argon measurements have been limited to the 36 and 40 peaks. Magnetic scanning was used with an 1500 V accelerated ion beam. Molecular flow was surely established, an important condition to make quantitative analysis without a calibration of the spectrometer. As a proof of the good performance of our instrument, we obtained for the A^{40}/A^{36} ratio in atmospheric Argon 294 ± 3, to be compared with the Nier's 296 ± 1, obtained with a carefully calibrated instrument. A typical mass spectrum of ours is reported in fig. 1.

Results of our analyses are reported in table I. The quoted error is mainly due to the reproducibility, as for this purpose some samples have been measured again after a few months.

TABLE I.

SOURCE	$[A^{40}/A^{36}]_{gas}/[A^{40}/A^{36}]_{atm.}$
FUMEROLES	
Agnano (Napoli)	1.15 (a)
Pozzuoli (Napoli)	1.12
Bullicame (Viterbo)	1.00
Montemiccioli (Volterra)	1.99
Rapolano (Siena)	1.26
SOFFIONI	
Larderello N. 1 (b) (Pisa)	1.22
Larderello » 2 »	1.19
Larderello » 3 »	1.16
Larderello » 4 »	1.24
Larderello » 5 »	1.28
Castelnuovo N. 1 »	1.12
Castelnuovo » 2 »	1.40
Serrazzano N. 1 »	1.60
Serrazzano » 2 »	1.71
Travale »	1.21
Sasso »	1.25
Lagoni Rossi »	1.45
Lago Tassinaie »	1.25
Monterotondo »	1.45

(a) Experimental error on the enrichment factor $\pm 4\%$.
(b) A progressive number has been used to identify different neighbor sources.

Discussion of the results.

With a glance at table I, one sees the observed enrichment to be sometimes very remarkable, compared with the usual variations of isotopic composition of elements in the earth.

The A^{40}/A^{36} ratio in all samples is never less than the atmospheric one, and this seems quite reasonable from the following considerations. The atmosphere of to-day is generally assumed to be completely of secondary origin [11], namely the result of the earth outgassing from the time when gravitational field and termal conditions were such to prevent gas excaping far from our planet. Although some outgassing still remains to-day, and volcanic phenomena are an example of it, the most important quantity of gases has been developed probably during the earth's solidification.

Let us consider Argon isotopes A^{40} and A^{36}. Due to the same chemical properties and the light mass difference, we can think they have had the same story in the process of earth outgassing. Also without any guess about the A^{40}/A^{36} value in the atmosphere at the beginning of the earth, one must say, as a result of K^{40} decay into A^{40}, that ratio has always been less in the atmosphere than in the inside of the earth. In other words, the A^{40}/A^{36} ratio in the atmosphere has alway been rising, but with some delay with respect to the inside of the earth.

Obviously one must always consider only the average value of the ratio A^{40}/A^{36} in the inside of the earth. In spite of our results, it can also happen that some natural gases have a η value less than one, and this is due to the non homogeneous Potassium distribution. The figures of table I show remarkable variations of η depending on the gas source.

We believe this is due to the non uniform geological constitution of the surface crust, to the different path of the gas coming to the surface and also to some air contamination inside the earth. It is difficult to day to explain these variation without a knowledge of the gas path, and also of data concerning η of the same source in different times.

To answer the question about the mechanism of A^{40} accumulation in the atmosphere, one should extend this kind of analysis to all the earth's surface, to know more about the quantity of natural gases excaping up to day. It is however interesting to point out that the Soffioni of Larderello supply about $4.4 \cdot 10^6$ grams of A^{40} per year, to be compared with $6.6 \cdot 10^{19}$ grams [12], which

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[11] H. JEFFREYS: The Earth (Cambridge, 1929), p. 312; H. BROWN: The Atmospheres of the Earth and Planets (Chicago, 1950), p. 260.

[12] F. A. PANETH: Neue Wege exact. Naturerk., pag. 1 (1939).

is the total A^{40} content in the atmosphere. Although it is not possible to think that such an intense outgassing happens all aroud the earth, the above figures allow us to believe that a remarkable amount of A^{40} is still flowing in the atmosphere.

Acknowledgment.

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RIASSUNTO

La composizione isotopica dell'Argon è stata misurata in un gran numero di fumarole e di soffioni italiani. Si è trovato un notevole arricchimento in A^{40}, sicuramente dovuto al decadimento del K^{40} contenuto nell'interno della Terra. Alla luce di queste misure viene considerato il problema della genesi dell'Argon atmosferico.