

## **GAS CARRIER AND DEGASSED MAGMATIC ROCKS AND THE PRIMORDIAL ATMOSPHERE\***

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The gas contents of granites and other continental plutonic rock samples were investigated and compared with a number of mantle rock samples and particularly with samples of the ophiolite sequence of the Troodos massif (Cyprus). The total volatile loss at 1000 °C was investigated. The gas composition was analysed by means of a quadrupole mass spectrometer after releasing the gases by crushing the samples in high vacuum at room temperature. In further experiments, release of CO<sub>2</sub> and volatile loss were determined as a function of temperature by means of derivatography. The high (about 9—15%) H<sub>2</sub>O and gas content of many mantle samples is compared to the always lower (1—2%) volatile content of crustal samples which seem to have been at least partially degassed in the course of geological evolution of the Earth's crust. It is assumed that the primordial atmosphere originated in the degassing of the crust. Gas carrier magmatic rocks in the deeper layers of the Earth, in the mantle still contain the components of the primordial atmosphere. Some of them are accessible and were analysed in this work.

### **Introduction**

The classification of igneous rocks in the title of this paper according to the gas content seems to be unusual compared with the conventional geological classification, according to which the silicate content, chemical composition, mineral structure, etc. are mainly considered in the highly complex magmatic differentiation. The science of igneous petrogenesis developed from the pioneering studies of Norman L. Bowen [1] considers these problems, many of which are still not properly understood.

The investigations reported here are concerned with the probable composition of the primordial atmosphere, a very interesting problem related to the origin of life. The rocks are regarded and investigated here but mainly as sources of the gases.

The title covers a hidden simple model theory which guided these experimental investigations. It is assumed that in the initial geological history of the Earth and the solar system, the aggregation of the Earth and terrestrial planets occurred from cold micrometeorites, chondrules, solid cosmic dust particles, etc. which contained adsorbed and confined gases brought from the cold cosmic space. At first, all material of the cold proto-Earth carried occluded gases and there was no hydrosphere or significant primordial atmosphere. After the aggregation, however, material on the

\* Dedicated to Prof. I. Tarján on his 70th birthday.

surface of the proto-Earth became degassed and the liberated gases retained by gravitation built up the primordial atmosphere.

Of course it must be emphasized that for two centuries very many theories have been proposed for the origin of the solar system. Any model theory, necessary for guidance in planning experimental measurements, is not entirely new since it contains at least parts of the earlier theories.

### **Selection of rock samples**

Igneous rock samples from different parts of the world were selected according to a global point of view, neglecting highly differentiated, fractionated samples of a composition very different from the average composition of the crust. The material of the continental crust, about 95% of which is made up of granites, is best represented by granite samples. Some very old granites were included as well, assuming that they suffered perhaps less differentiation and so are probably less degassed. Some other igneous continental rocks were investigated as well. Basalts originate from and are derived by partial melting of the upper mantle. Only a limited number of ophiolites have been obtained. The Troodos (Cyprus) ophiolite sequence was very particularly investigated, because it represents probably the least disturbed and best investigated mantle material, together with the overlying sequence of crustal rocks.

In the course of geological evolution the Earth's crust suffered very many distortions, (subductions, orogenesis, metamorphosis, etc.). Its thickness under the continents is varied (tens of kilometres), however, the crust under the ocean bottom, amounting to about 70% of the total surface of the Earth, is about 6—7 km thick and more uniform.

The investigation of ophiolites shows that they are ancient parts, slabs of the oceanic crust and upper mantle uplifted to the surface by tectonic movements thus they are easily accessible for observations and sampling for laboratory investigations. The ophiolite sequence of the Troodos massif of Cyprus is one of the least deformed ophiolites and also the one most extensively studied and understood [2]. The lowest layer of oceanic crustal rock, gabbro is well exposed there and so are the uppermost layers of the mantle, the serpentinized ultramafic rocks of dunite and harzburgite. The Mohorovicic discontinuity [6] is the separating boundary layer between the deepest crustal layer of gabbro (or gabbroids) and the uppermost layer of the mantle dunite, or harzburgite, if the sequence is ideally undisturbed.

The investigations briefly reported here about the gas content of these rocks demonstrate that there is a discontinuity in it too, the gas content of crustal rocks being about one order of magnitude lower than that of the mantle rocks on the underlying side of the Moho. Besides the Troodos sequence, a kimberlite and a number of continental granites and some other igneous rocks (e.g. some ultramafic rocks from Hungary) were studied. A more detailed report will be published later [10].

## Experimental results

The total volatile content was determined simply by powdering the sample in an agate mill to a grain size of less than  $200\ \mu$  and after drying at  $100\ ^\circ\text{C}$ , heating for 2 hours at  $1000\ ^\circ\text{C}$ . (The derivatographic investigation demonstrates that  $1000\ ^\circ\text{C}$  is enough for the rapid release of the volatiles from a powdered sample). The weight loss is expressed in per cent and includes practically all the water and real gas volatiles content.

Fig. 1 demonstrates the distribution of the rock samples regarding total volatile loss. Each square represents a sample.

The investigated number of granites and other plutonic rocks from several continents, including some of the oldest granites of the Earth, have a low volatile content of 1.0 weight % mean value, with min. 0.3% and max. about < 3%. The few gabbros including the Troodos sample fall into this interval. However serpentinized peridotite rocks from Troodos have a high volatile content (between 8.6—15%) and so has a fresh (unweathered) serpentinized kimberlite from de Beers mine, Kimberley, a high volatile content of 13.2%. Ultramafic rocks from Hungary contain about similarly high volatiles. The volatile contents of a number of basalts range between these two extreme groups. Basalts situated now in the crust derived and rose actually from the upper mantle. We can conclude from Fig. 1 that the volatile content of the serpentinized peridotite rocks from the mantle investigated here is high and that of all investigated igneous rocks of the crust including the gabbro immediately above the Moho is low. Basalts are somewhat less degassed than granites.

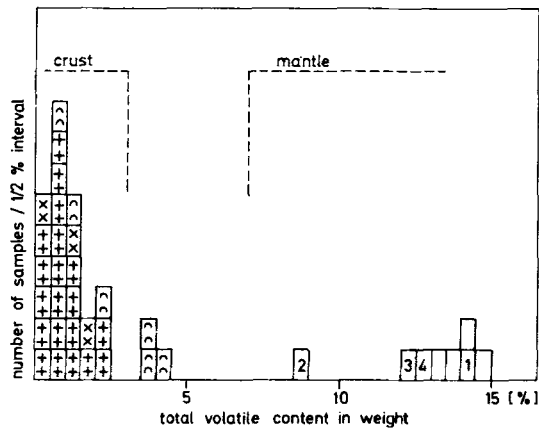


Fig. 1. Comparison of the total volatile loss in weight per cent between crustal rocks and ultramafic mantle rocks. Each square represents a sample. Signs: 1 Dunite (Troodos mts), 2 Harzburgite (Troodos mts), 3 Kimberlite fresh (Kimberley), 4 Serpentinized ultramafic (Lotus Colona, Calif. USA),  $\square$  Serpentinized ultramafics (Hungary),  $\oplus$  Granite, gneiss, amphibolite gneiss, granodiorite,  $\square$  Andesites, basalt, lavas,  $\otimes$  Gabbro

The abrupt change of the gas content from the upper mantle (dunite, harzburgite) to the crustal gabbro is very significant. A strong degassing occurs when hot mantle substance migrates across the Moho into the crust and differentiates by magmatic events.

The composition of the gas content was investigated by means of a quadrupole mass spectrometer (QMS), in a different type of experiment. The high sensitivity of the QMS enabled us to measure just a small sample of the gases released from the rocks without heating, by crushing them in a high vacuum mortar between hard tungsten-carbide steel dies. When crushing a 0.6 g sample of rock of about 0.6 mm grain size to small grains, enough volatiles are liberated to determine the gas content in the original composition as it was in thermochemical equilibrium in the rock without any chemical reaction between the gases by heating. The obtained composition justified the cold crushing, because much of  $H_2$  and  $CH_4$  strongly reducing gases have been liberated, together with  $H_2O$ ,  $N_2$  and  $CO_2$ . They would have been partly reacted at  $1000^\circ C$ . The molecular composition between  $M = 1-50$  was investigated. The whole analysis was carried out in an ultra high vacuum apparatus, at  $10^{-6}$  mbar. The background of the equipment was about  $1-3 \cdot 10^{-8}$  mbar.

The measurements were carried out under dynamic conditions. After liberating the gases by crushing, a needle valve of the mortar was opened and regulated so that a pressure of  $1 \cdot 10^{-6}$  Torr was established in the QMS under continuous evacuation by means of a turbomolecular pump. Full description of the apparatus and measuring technique will be published elsewhere [3].

Fig. 2 shows the mass spectrum of the gases of dunite from Troodos.

The following can be said concerning the composition of gas content liberated by cold crushing: the QMS mass spectra demonstrate that the amount of water is overwhelming; free oxygen is never present;  $H_2$ ,  $CH_4$ ,  $CO_2$ ,  $N_2$  are rather abundant;

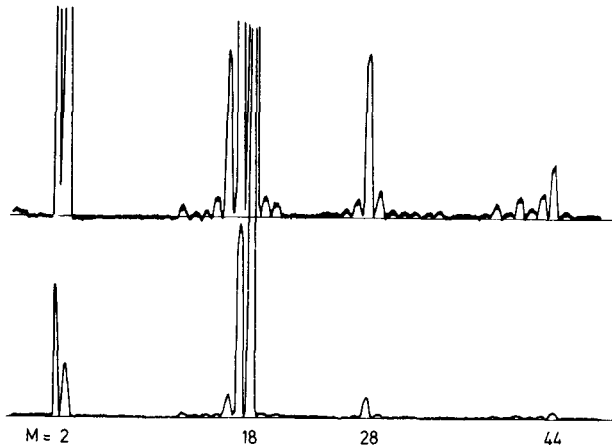


Fig. 2. QMS spectrum of gases in dunite (Troodos mts, Cyprus), released by cold crushing. Ordinate: Electrometer readings, with two (1:8) sensitivities; Abscissa: Molecular weight

argon and some traces of organic components can be observed within the investigated range of molecular weight  $M = 1-50$ . Evaluation after the necessary calibration of the QMS and corrections for molecular fragments by ionization result in the following approximate gas composition as the mean value  $\pm$  standard deviation of 16 dunite samples, in volume units, related to  $N_2 = 100$ :  $CO_2 = 80 \pm 10$ ;  $CH_4 = 50 \pm 4$ ;  $H_2 > 100$ . (N.B.: the scattering between the samples is considerable because probably at least a part of the gases is contained in microbubbles within the mineral grains and so they are not evenly distributed.)

The gas is a reducing one and perhaps might be considered to approximate qualitatively the ancient reducing primordial atmosphere. Similar investigations were carried out by the author on granites, etc. earlier [7, 8]. The determination of the hydrogen content was more inaccurate in these measurements because the overwhelming amount of  $H_2O$  molecules gave a great number of fragmented ions, in addition to  $(H_2O)^+ : H^+$ ,  $(OH)^+$ ,  $O^+$ ,  $H_2^+$ . The hydrogen inclusion in the rocks is liberated by the crushing in the form of  $H_2$  molecules which are ionized in the QMS to  $H_2^+$  and the fragment ion  $H^+$ . The disturbing background of hydrogen fragments originating from water molecules was eliminated in another series of measurements. Water vapour was frozen out by liquid nitrogen trap so it appeared only in a small extent in the spectrum. Of course  $CO_2$  was frozen out as well. The correction due to the water ion fragments became much smaller and less disturbing. This was very favourable for the determination of hydrogen content and for the determination of methane content as well. We obtained in these measurements the following values for  $H_2$  and  $CH_4$  in the dunite sample related to  $N_2 = 100$ :

$$\begin{aligned} CH_4 &= 47 \pm 5, \\ H_2 &\sim 100 - 500, \end{aligned}$$

There is still a source of uncertainty in the value of hydrogen content because of the higher diffusing speed of  $H_2$  molecules in a high vacuum. When the needle valve of the crushing mortar is opened the  $H_2$  is diffusing much quicker into the QMS than the other gases. In the first seconds its abundance seems to be about 500 related to  $N_2 = 100$ . It is, however, very quickly extracted from the system by the turbomolecular pump and then after about 90 seconds its abundance is only about equal to  $N_2$ . A more accurate determination of  $H_2$  would be possible only in a closed vacuum system in diffusion equilibrium. The QMS used in this experiment was not suitable for long measurements with a closed system since, because of background outgassing problems, the ultrahigh vacuum cleanliness was limited.

In addition the Troodos and other mantle samples were investigated by derivatography, developed by F. Paulik et al [4, 5]. About 300 mg powdered samples were heated gradually by  $10^\circ C/min$  up to  $1000^\circ C$  in a slow stream of  $N_2$  (free of  $CO_2$  and  $O_2$ ). The change of weight and release of heat (change of enthalpy) were continuously and automatically recorded. The automatic quantitative analysis of liberated  $CO_2$  as a function of temperature offered further significant information.

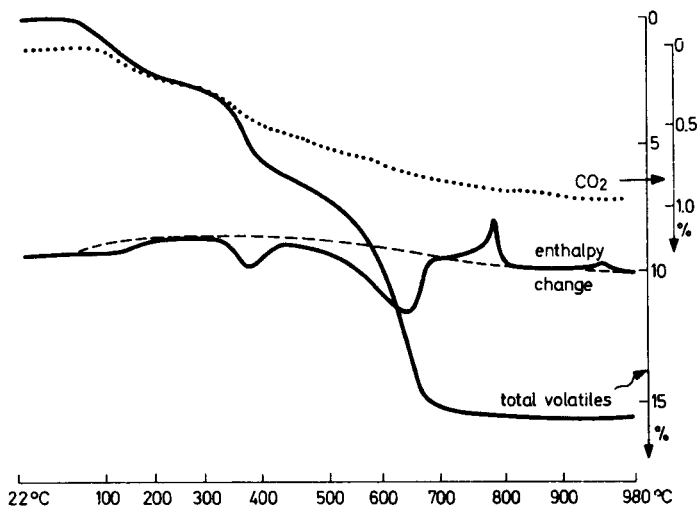


Fig. 3. Derivatographic investigation of dunite (Troodos mts, Cyprus). Ordinate: Loss of total volatiles in weight %, loss of  $\text{CO}_2$  in weight %, and change of enthalpy; Abscissa: temperature, rate of increase  $10^\circ\text{C}/\text{min}$

This method gives information about the manner of fixation of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and mineral transformations in the rocks, further about the total volatile loss as a function of temperature.

In Fig. 3 the results of derivatographic investigation of a Troodos dunite are demonstrated. It can be seen that the  $\text{CO}_2$  was not chemically fixed as a carbonate. It is gradually released by increasing the temperature, no definite decomposition temperature is observable. The  $\text{CO}_2$  content amounts to 0.94% of weight. However, at least a part of the water is fixed into the mineral structure (serpentine). Liberation of  $\text{H}_2\text{O}$  occurs at about  $340^\circ\text{C}$  with disappearance of heat. This water belongs to  $\text{Mg}(\text{OH})_2$  which is transformed into  $\text{MgO}$  by liberating one molecule of water which amounts to about 2.2% weight. Another release of  $\text{H}_2\text{O}$  of about 7.2% of weight occurs at a temperature of about  $660^\circ\text{C}$  again with significant heat disappearance. However, if we follow the change of enthalpy curve, we see a sudden liberation of heat at  $780^\circ\text{C}$ . This is the well known transformation of the crystal structure of chrysotile into olivine. A similar transformation was observed on chrysotile asbestos (Troodos), mined on a large scale in the Troodos massif, and on the other peridotites as well. Kimberlite liberates  $\text{CO}_2$  from  $500\text{--}600^\circ\text{C}$  on, so this seems to be chemically fixed as carbonate, probably carbonatite.

About 95% of the continental Earth crust consists of granites. The significant number of granite and other plutonic rock samples investigated here are obtained from several continents, from different parts of the Earth's crust and have different ages. Their volatile content is always small varying between tight limits of 0.3% and 3%, the mean value of 1.0% approximates the average total volatile content of the continental

magmatic crust. Few gabbro samples have been investigated but they fall into this range. Only a single ophiolite sequence was investigated but the Troodos massif is the least disturbed among the known not numerous ophiolite occurrences. Concerning the mantle rocks, the number of samples of dunite and harzburgite, further chrysotile asbestos from Troodos and fresh kimberlite from Kimberley (South Africa) and some serpentized ultramafic rocks from Hungary is small but it is generally assumed that the composition of the upper mantle is more uniform, better averaged than that of the very differentiated crustal rocks. Dunite and harzburgite represent the oceanic mantle from a depth of about 6 km to about some ten km. From the well known phase changes of diamond-graphite and quartz it is known that kimberlite must originate at a depth of between 100—300 km [9]. The geographical distance between Cyprus and Kimberley is about 7000 km. The few investigated mantle samples originate from depths between 6 and >100 km, and a distance of 7000 km and have a similar total volatile content of the same magnitude.

Although there are some rocks from the upper mantle which are degassed and some xenoliths (inclusions of some small peaces of mantle rocks into magma) carried quickly to the surface by molten magma are degassed, it seems that the undisturbed mantle can be regarded as a gas carrier. Explorations of the sub-oceanic mature crust and mantle by the originally planned bore-hole (Mohole) project or a much easier exploratory bore-hole into the uplifted Troodos complex will justify this supposition. It can be assumed that the present crust was in the earlier period of the evolution of the Earth a gas carrier like the mantle still is today. Its degassing produced the present hydrosphere and atmosphere.

The composition of the primordial atmosphere was comparable to the gas content of the gas carrier mantle samples. It did not contain any free  $O_2$  at all and it was strongly reducing because of its abundant  $H_2$  and  $CH_4$  content. The  $H_2$  content might have gradually escaped into space because gravitation could not retain it. This composition of the primordial atmosphere was suitable for the evolution of organic molecules and finally life by means of the free energy of the ultraviolet radiation of the sun.

### Acknowledgements

The author expresses his best thanks for collaboration to Colleagues of this Institute and for valuable discussion to geologists, further to the donators of some of the samples. The author is particularly grateful to Dr. J. Paulik and Dr. F. Paulik of the Institute for General and Analytical Chemistry, Technical University of Budapest, who carried out the derivatographic determinations of Troodos mantle rocks and other peridotites by their home-developed highly precise automatic derivatographs.

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