Lithium and Halogens in Lunar Samples

G. Dreibus, B. Spettel and H. Wanke

Phil. Trans. R. Soc. Lond. A 1977 **285**, 49-54
doi: 10.1098/rsta.1977.0042

Phil. Trans. R. Soc. Lond. A. **285**, 49–54 (1977)
Printed in Great Britain

Lithium and halogens in lunar samples

By G. Dreibus, B. Spettel and H. Wänke
Max-Planck-Institut für Chemie (Otto-Hahn-Institut),
Abteilung Kosmochemie, Mainz, Germany

Lithium and the halogen elements F, Cl, Br and I have been measured in soils, breccias and rock samples from all Apollo missions. With the exception of the anorthosites, the fluorine content of the lunar samples is in the same range as for C1 chondrites. Contrary to fluorine the other halogen concentrations show large variations. The lowest concentrations are found in the mare basalts of Apollo 15 and 17, the highest in some highland breccias.

Lithium correlates well with some of the incompatible elements in both mare basalts and 'KREEP'-containing highland soils and breccias. From the observed ratios it is evident that in the bulk composition of the Moon Li is neither enriched nor depleted; it belongs to the group of non-refractory elements.

From the correlation of Li with some refractory elements (Be, La, etc.) a value of 50:50 for the refractory to non-refractory portion of the Moon is inferred without any further assumption, thus confirming previous estimates of Wänke *et al.* (1974*a*, 1975).

INTRODUCTION

Lithium and the halogens have been measured in both lunar mare and highland samples. Lithium, Cl, Br and in a few cases I were determined with neutron activation. Pyrohydrolysis was applied for the extraction of all the halogens. Lithium was measured via the reactions

$$^{6}\mathrm{Li}\ (n,\alpha)\ \mathrm{T};\quad {}^{16}\mathrm{O}\ (t,n)\ {}^{18}\mathrm{F}.$$

After γ-ray counting of ^{18}F, ^{38}Cl, ^{82}Br and ^{128}I, F was determined with a specific ion electrode. A comparison of our data on Li with those obtained by isotopic dilution method by Philpotts *et al.* (1974) proves the applicability of our method (see Wänke *et al.* 1974*a*).

HALOGENS IN LUNAR SAMPLES

The results of our measurements on the various types of lunar samples are summarized in table 1. In general, the data obtained are in the same range as those given by Jovanovic & Reed (1973, 1974). Figure 1 gives an illustration of the results of our measurements. As it can be seen, F is the least variable one of these elements. Except for the lunar anorthosites (65315) and the anorthosite-rich highland samples F concentrations are similar to that in C1 chondrites.

Chlorine, Br and I show large variations. The lowest concentrations are found in the mare basalts. Highland samples have highly variable concentrations of these elements. Some but not all of the samples with high concentrations of Cl, Br and I are also high in other volatile elements. As it is demonstrated by Wänke *et al.* (1974*a*, 1975), all the highland samples contain large amounts of a primary component. However, we do not observe any correlation between the content of Cl, Br and I and the amount of the primary component present in the samples.

We believe therefore that these halogens which were probably exhaled from the lunar interior were added at a late stage in the form of a vapour phase condensing on these highland soils and breccias, Meyer *et al.*(1975) have already presented evidence for such a process from investigations on Pb and other volatiles. A similar process might be responsible for the slight enrichment of these halogens in mare soils relative to mare basalts. We should also note that in all cases the three elements Cl, Br and I do not fractionate at all from each other. The same behaviour is also found for terrestrial rocks and achondrites, of which BCR-1 and the achondrite Juvinas are included in figure 1 for comparison.

TABLE 1. RANGE OF THE CONCENTRATIONS OF Li, F, Cl, Br AND I IN LUNAR SAMPLES AS DERIVED FROM OUR MEASUREMENTS (PARTS/10^6)

The respective concentrations in Orgueil C1 chondrite as determined by us are also listed. Here our values for Cl, Br, and I fall within the range of previous data from the literature (see Mason 1971). In the case of F our value (Dreibus *et al.* 1973) lies considerably below the older value of 158 parts/10^6 obtained by Reed (1964). A similarly low F content of 74 parts/10^6 for Orgueil was recently reported by Goldberg *et al.* (1974).

	Li	F	Cl	Br	I
mare rocks (Apollo 11)	11–14	66–84	15–21	0.04–0.12	~ 0.08
mare rocks (Apollo 15 a.17)	6.2–8.3	27–78	3.5–6.0	0.01–0.03	~ 0.01
mare soils and breccias	8.4–10.7	58–60	12, 3–26	0.09–0.20	0.01–0.03
highland soils	6.9–24.8	14–71	10–270	0.04–0.9	0.01–0.07
14163 (kreep)	31†	145	40	—	—
Orgueil C1	1.3†	52	580	2.68	0.548

† The Li value for 14163 was taken from Schnetzler *et al.* (1971) and that for Orgueil from Nichiporuk & Moore (1970).

LITHIUM AS A CORRELATED ELEMENT

As it can be seen from figure 2 Li correlates quite well with other incompatible elements. Normalized to C1 concentrations the La/K ratio which is almost constant in practically all lunar samples has a value of 30. Hence, on the Moon La is enriched by this factor relative to K. In the paper of Wänke *et al.* (1976) of this conference, a depletion factor of 3 was estimated for K, leading to an absolute enrichment of La by a factor of 10. As the same value of 10 is found for the La/Li ratio (normalized to C1), Li can neither be enriched nor be depleted in the Moon or in other words: Lithium does not condense together with the refractory elements (Ganapathy & Anders 1974), but follows the Mg, Fe-silicates. The Mg, Fe-silicates represent the non-refractory portion of the Moon and Li is present in them in chondritic abundance.

Of course, we wanted to confirm these results about the condensation behaviour of Li obtained from element correlations in lunar samples involving several not strictly proven assumptions. Therefore, we have determined Li in an Allende inclusion, in which according to the analysis carried out in our laboratory (Wänke *et al.* 1974*b*) the refractories were highly enriched and which had a low Fe content of 1.6 %. In a 20 mg aliquot of this inclusion we found a Li concentration of 1.2 ± 0.4 parts/10^6. Owing to the small amount of the sample the error is quite large, but it is clear that Li is definitely not enriched in this inclusion. Hence, we have proven that Li does not belong to the group of refractory elements.

As Li is neither depleted nor enriched on the Moon, but relative to Mg it is present in C1 abundance, this element can be used to estimate the concentration of other elements which

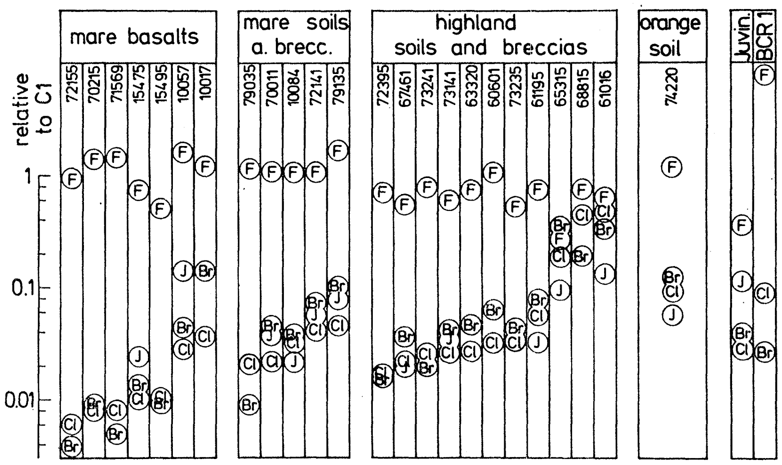

FIGURE 1

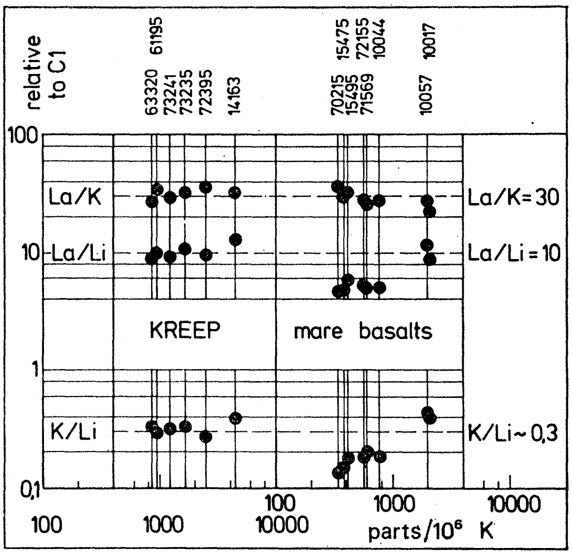

FIGURE 2

FIGURE 1. Halogen concentrations in some lunar samples relative to C1 chondrites.

FIGURE 2. La/K, La/Li and K/Li ratios in lunar mare and highland samples normalized to C1.

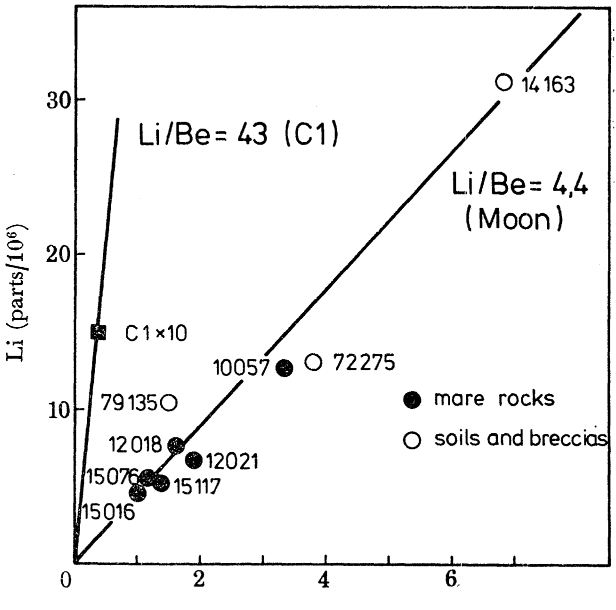

FIGURE 3

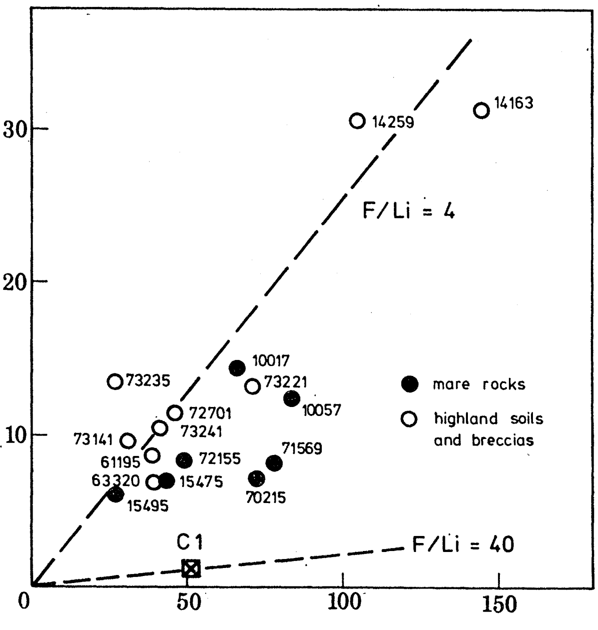

FIGURE 4

FIGURE 3. Li against Be. Be values: 10057 Annell & Helz (1970); 12018 and 12021 Cuttitta *et al.* (1971); 14163 Rose *et al.* (1972); 15016, 15076 and 15117 Cuttitta *et al.* (1973); 72275 and 79135 Rose *et al.* (1974). Li values: 10057 this laboratory; 12018 Schnetzler & Philpotts (1971); 12021 Cuttitta *et al.* (1971); 14163 Schnetzler & Nava (1971); 15016, 15076 and 15117 Cuttitta *et al.* (1972); 72275 Hubbard *et al.* (1974), 79135 this laboratory.

FIGURE 4. Li against F in lunar samples.

correlate with Li. (It is preferable to normalize to Mg instead of Si, because the fraction which condenses with the refractories is larger for Si than it is for Mg.)

In lunar samples Li correlates very well with Be which also has a small ionic radius (figure 3). Beryllium is a highly refractory element and indeed the Li/Be ratio found for lunar samples is also about a factor of 10 lower as the C1 ratio. Hence, Be like the other refractory elements must be enriched on the Moon by this factor of 10 relative to C1 chondrites. From a F/Li diagram (figure 4) we infer that F is depleted on the Moon by about a factor of 10.

Bulk composition of the Moon

The Li/Be ratio or any other ratio of Li to a refractory element which correlates well with Li might be superior for the evaluation of the lunar bulk composition compared to the K/La ratio or K/Ba ratio, etc., as it is very difficult to estimate the depletion of K with certainty. Contrary to the heavier alkali elements, Li has certainly not been depleted relative to Mg due to its low volatility. This was also confirmed experimentally by Gibson & Hubbard (1972).

One can use La (or Be, or Zr) as a measure of the abundance of the refractories. In a similar way Li can serve as a direct measure for the abundance of the non-refractories. On an absolute scale the non-refractory portion of the primary component observed in the lunar highlands contains 18.8 % Mg, i.e. exactly twice the C1 concentration. Hence, the concentration of Li in this portion must also be twice the C1 value. According to the experimental evidence from Allende inclusions, the early condensates or high temperature condensates – i.e. the refractory portion of the Moon – are about 20 times enriched in nearly all refractory elements. From the observed C1 normalized Be/Li or La/Li ratio of 10, a 50:50 ratio of the refractory to non-refractory portion in the bulk Moon is inferred.

Hence, for the bulk Moon we find a much higher abundance of refractories as for the matter observed in the lunar highlands, for which Wänke *et al.* (1975) computed a value of 21 % from a two-component mixing diagram.

group	indicator	elements
refractories	La or Be	Al, Ca, Ti, (Mg, Si) Sc, V, Sr, Y, Zr, Nb, Mo, Ru Rh, Ba, REE, Hf, Ta, W Re, Os, Ir, Pt, Th, U. not fractionated
non-refractories	Li	Mg, Fe (FeO), Si, Cr not fractionated
moderately volatiles	K	Mn, Na, Rb, Cs slightly fractionated

Knowing the ratio of the refractory to the non-refractory portion of the Moon the elemental composition can be evaluated as previously (Wänke *et al.* 1975, 1976, this volume).

We like to stress once again that it is not possible to explain the elemental composition of the Moon by a *depletion* of the volatile alkali elements, but that the refractory elements have to be *enriched* to a level of 10 times C1 concentrations.

THE EARTH – MOON SYSTEM

As it was pointed out in the paper of Wänke *et al.* (this volume), W correlates well with La in all lunar samples, but the W/La ratio lies about a factor of 17 below the chondritic ratio indicating that 94 % of W, which is a truly refractory element with strong siderophile tendencies, was removed from the silicates by metallic iron. It was also shown that the terrestrial samples and the achondrites plot along the same correlation line as the lunar samples in spite of the fact that the Earth is thought to contain about 30 % of metallic iron, while the lunar metal content is probably at least about a factor of 10 lower.

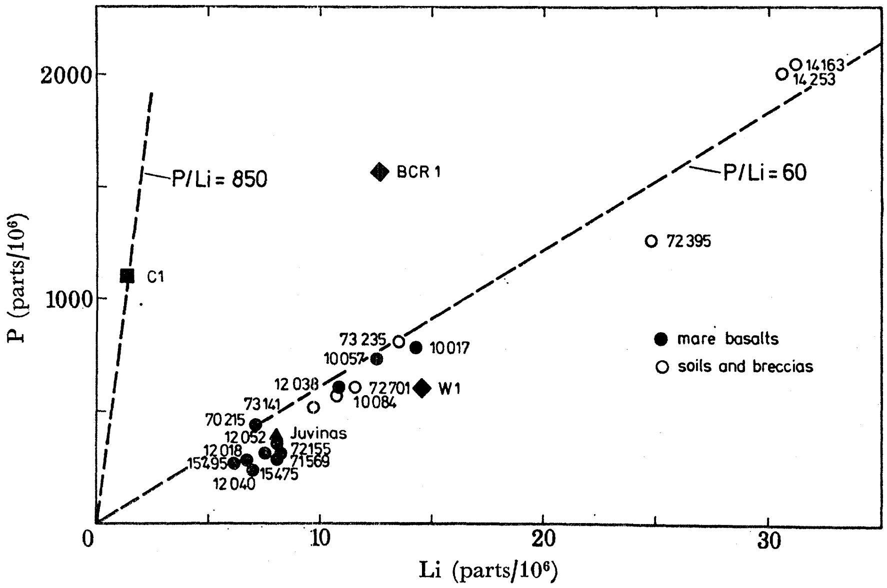

FIGURE 5. P against Li. P values: 10017 and 10084 Compston *et al.* (1970), 10057 Engel & Engel (1970), 12018 Cuttitta *et al.* (1971), 12038, 12040 and 12052 Compston *et al.* (1971), all other samples this laboratory Wänke *et al.* (1975). Li values: 12018, 12038, 12040 and 12052 Schnetzler & Philpotts (1971), 14163 and 14259 Schnetzler & Nava (1971); all other samples this laboratory Wänke *et al.* (1975).

A similar behaviour is found from the Li/P correlation (figure 5). Relative to the C1 ratio P seems to be depleted in the lunar silicates by about a factor of 14, the achondrite Juvinas and terrestrial samples show a depletion of the same order of magnitude. Evidently, in all these objects P might have been removed to a large extent together with metallic iron.

We have now an increasing number of geochemical observations which have considerable bearing on the theories of the origin of the Moon and the Earth–Moon system.

(1) The Moon is much richer in refractory elements as compared to the Earth. Nevertheless the Moon consists of about 50 % of Mg, Fe-silicates, but can have only very little metallic iron.

(2) The Earth and the Moon have been depleted in volatile and moderately volatile elements.

(3) Among correlated elements those with considerable siderophile tendencies show equal ratios to purely lithophile elements for the Moon, the Earth and the achondrites (W/La, P/Li).

(4) According to the observation of Clayton & Mayeda (1975), Earth, Moon and achondrites lie on the same oxygen isotope fractionation line.

(5) The total Fe content of the Earth is higher than that of chondrites.

Without having a firm conclusion ourselves, we like to stress that models which allow the metal-silicate fractionation to take place within the proto-Earth, and the Moon being accreted from the material condensed from a 'planetary nebula' formed by evaporation of a considerable fraction of the proto-Earth (Ringwood 1960, 1970; Wise 1963, 1969; O'Keefe 1969) would resolve these constraints.

References (Dreibus, Spettel & Wänke)

Annell, C. S. & Helz, A. W. 1970 *Proc. Apollo* 11 *Lunar Sci. Conf. Geochim. cosmochim. Acta* **2**, 991–994.

Clayton, R. N. & Mayeda, T. K. 1975 Preprint.

Compston, W., Berry, H., Vernon, M. J., Chappell, B. W. & Kaye, M. J. 1971 *Proc. Lunar Sci. Conf.* 2nd, *Geochim. cosmochim. Acta* **2**, 1471–1485.

Compston, W., Chappell, B. W., Arriens, P. A. & Vernon, M. J. 1970 *Proc. Apollo* 11 *Lunar Sci. Conf. Geochim. cosmochim. Acta* **2**, 1007–1027.

Cuttitta, F., Rose, H. J., Jr, Annell, C. S., Carron, M. K., Christian, R. P., Dwornik, E. J., Greenland, L. P., Helz, A. W. & Ligon, D. T., Jr. 1971 *Proc. Lunar Sci. Conf.* 2nd, *Geochim. cosmochim. Acta* **2**, 1217–1229.

Cuttitta, F., Rose, H. J., Jr, Annell, C. S., Carron, M. K., Christian, R. P., Ligon, D. T., Jr, Dwornik, E. J., Wright, T. L. & Greenland, L. P. 1973 *Proc. Lunar Sci. Conf.* 4th, *Geochim. cosmochim. Acta* **2**, 1081–1096.

Dreibus, G., Palme, H. & Wänke, H. 1973 *Meteoritics* **8**, 29.

Engel, A. E. J. & Engel, C. G. 1970 *Proc. Apollo* 11 *Lunar Sci. Conf. Geochim. cosmochim. Acta* **2**, 1081–1084.

Ganapathy, R. & Anders, E. 1974 *Proc. Lunar Sci. Conf.* 4th, *Geochim. cosmochim. Acta* **2**, 1181–1206.

Gibson, E. K., Jr & Hubbard, N. J. 1972 *Proc. Lunar Sci. Conf.* 3rd, *Geochim. cosmochim. Acta* **2**, 2003–2014.

Goldberg, R. H., Burnett, D. S., Furst, M. J. & Tombrello, T. A. 1974 *Meteoritics* **9**, 347–348.

Hubbard, N. J., Rhodes, J. M., Wiesmann, H., Shih, C.-Y. & Bansal, B. M. 1974 *Proc. Lunar Sci. Conf.* 5th, *Geochim. cosmochim. Acta* **2**, 1227–1246.

Jovanovic, S. & Reed, G. W., Jr. 1973 *Proc. Lunar Sci. Conf.* 4th, *Geochim. cosmochim. Acta* **2**, 1313–1324.

Jovanovic, S. & Reed, G. W., Jr. 1974 *Proc. Lunar Sci. Conf.* 5th, *Geochim. cosmochim. Acta* **2**, 1685–1701.

Mason, B. 1971 New York: Gordon & Breach,

Meyer, C., Jr, McKay, D. S., Anderson, D. H. & Butler, P., Jr. 1975 *Lunar Sci.* **6**, 560–562.

Nichiporuk, W. & Moore, C. B. 1970 *Earth Planet. Sci. Lett.* **9**, 280–286.

O'Keefe, J. A. 1969 *J. geophys. Res.* **74**, 2758–2767.

Philpotts, J. A., Schuhmann, S., Kouns, C. W., Lum, R. K. L. & Winzer, S. 1974 *Proc. Lunar Sci. Conf.* 5th, *Geochim. cosmochim. Acta* **2**, 1255–1267.

Reed, G. W., Jr. 1964 *Geochim. cosmochim. Acta*, **28**, 1729–1743.

Ringwood, A. E. 1960 *Geochim. cosmochim. Acta* **20**, 241–259.

Ringwood, A. E. 1970 *Earth Planet. Sci. Lett.* **8**, 131–140.

Rose, H. J., Jr, Cuttitta, F., Annell, C. S., Carron, M. K., Christian, R. P., Dwornik, E. J., Greenland, L. P. & Ligon, D. T., Jr. 1972 *Proc. Lunar Sci. Conf.* 3rd, *Geochim. cosmochim. Acta* **2**, 1215–1229.

Rose, H. J., Jr, Cuttitta, F., Berman, S., Brown, F. W., Carron, M. K., Christian, R. P., Dwornik, E. J. & Greenland, L. P. 1974 *Proc. Lunar Sci. Conf.* 5th, *Geochim. cosmochim. Acta* **2**, 1119–1133.

Schnetzler, C. C. & Nava, D. F. 1971 *Earth Planet. Sci. Lett.* **11**, 345–350.

Schnetzler, C. C. & Philpotts, J. A. 1971 *Proc. Lunar Sci. Conf.* 2nd, *Geochim. cosmochim. Acta* **2**, 1101–1122.

Wänke, H., Baddenhausen, H., Palme, H. & Spettell, B. 1974*b* *Earth Planet. Sci. Lett.* **23**, 1–7.

Wänke, H., Palme, H., Baddenhausen, H., Dreibus, G., Jagoutz, E., Kruse, H., Spettel, B., Teschke, F. & Thacker, R. 1974*a* *Proc. Lunar Sci. Conf.* 5th, *Geochim. cosmochim. Acta* **2**, 1307–1335.

Wänke, H., Palme, H., Baddenhausen, H., Dreibus, G., Jagoutz, E., Kruse, H., Palme, C., Spettel, B., Teschke, F. & Thacker, R. 1975 *Proc. Lunar Sci. Conf.* 6th, *Geochim. cosmochim. Acta* **2**, 1313–1340.

Wise, D. U. 1963 *J. geophys. Res.* **68**, 1547–1554.

Wise, D. U. 1969 *J. geophys. Res.* **74**, 6034–6045.