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H. Wanke, H. Palme, H. Baddenhausen, G. Dreibus, H. Kruse and B. Spettel

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Element correlations and the bulk composition of the Moon

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

A great number of element correlations have been observed in lunar samples. It is known from theoretical and experimental studies that in the solar nebula the elements condensed in groups according to their condensation temperatures and chemical affinities. One of these groups – the refractory elements – is represented by the early condensates or high temperature condensates (h.t.c.). From element correlations and group relations we estimate the bulk Moon to contain about 50 % of h.t.c.; the other 50 %, the non-refractory portion, consists mainly of (Mg, Fe)-silicates and minor phases of about chondritic composition.

Recently we have found strong evidence that most of the lunar highland samples represent mechanical mixtures of a differentiated (feldspathic) lunar component and a primary component from the last accretion stage of the Moon. The contribution of the h.t.c. in this primary material is estimated to 21 %. Hence, an inhomogeneous accretion of the Moon is indicated. After the formation of a highly refractory core relatively more and more non-refractory material was added until the Moon reached its final mass. The composition of the primary matter observed in the lunar highlands gives us an important clue to the composition of the non-refractory portion of the Moon and thus leads to a more reliable estimation of the lunar bulk composition.

ELEMENT CORRELATIONS

In the course of the lunar investigations the discovery of the so-called correlated elements is of general geochemical importance. Correlated elements are pairs of elements which in spite of large variations of their absolute concentrations in different lunar samples always occur in constant abundance ratios.

Most of the conclusions of this paper are based on data obtained from the multi-element analyses programme carried out in our laboratory (Wänke *et al.* 1973, 1974*a*, 1975). Of course, in addition to our data, the results of all other groups working on lunar sample analyses were taken into account.

Figure 1 shows the correlation of Mn with Fe which was first pointed out by Laul *et al.* (1972). The basis for this correlation lies in the fact that Mn^{2+} can easily replace Fe^{2+} in most minerals in question, because of the close similarity of the ionic radii of these two ions. All lunar samples have an Fe/Mn-ratio close to 80 and we have good reasons to suppose that this ratio holds for the whole Moon. Terrestrial samples plot on a different correlation line, indicating that the Moon cannot in a simple way be a broken-off piece of the Earth.

Another group of elements which always appear in more or less constant element ratios is formed by those trace elements which have ionic radii either too large or too small to be readily accepted by the dominant minerals. They are therefore also called incompatible elements.

An example of such a pair is U and La (figure 2). Both elements have large ionic radii and

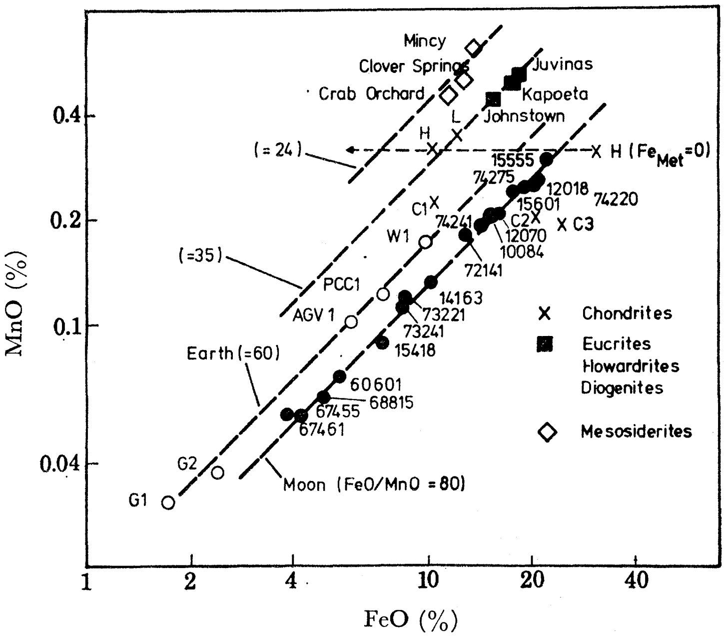

FIGURE 1. MnO-FeO correlation noticed first by Laul *et al.* (1972) for lunar samples. A similar correlation is observed for terrestrial and meteoritic samples. By oxidation of metallic iron the data point of a material with a composition of an ordinary H-group chondrite (marked H) will move along the horizontal dashed line.

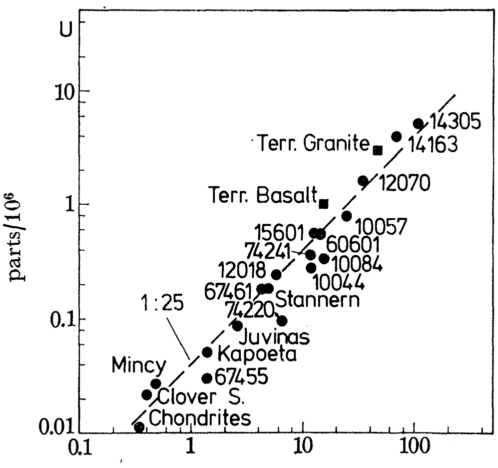

FIGURE 2

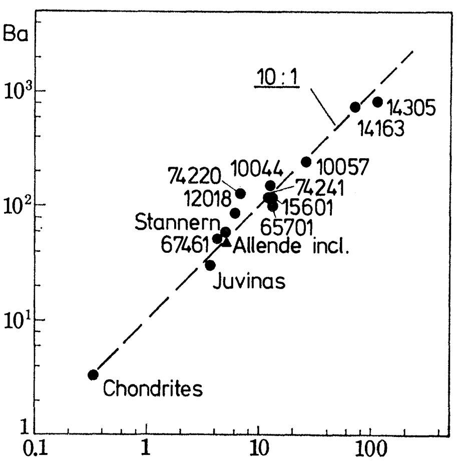

FIGURE 3

FIGURE 2. U against La. Lunar samples, terrestrial samples, achondrites (Stannern, Juvinas, Kapoeta), mesosiderites (Mincy, Clover Springs) and chondrites plot along the same correlation line.

FIGURE 3. Ba against La. As for the U-La correlation an identical ratio is observed for all objects plotted.

both are highly refractory. It is important to note that the chondritic value falls on the lunar correlation line as well as the data points for terrestrial samples and those for achondrites and mesosiderites.

It was already pointed out several years ago by Larimer & Anders (1970) and Anders (1971) that the refractory elements did not fractionate from each other during condensation and accretion of the parent bodies of the chondrites. The essentially constant and chondritic ratios of incompatible refractory elements (like, for example, U/La, Ba/La, see figures 2 and 3) clearly demonstrate that

(*a*) the incompatible refractory elements and probably also the other refractory elements did not fractionate from each other during condensation and accretion of the matter that formed the Moon;

(*b*) the incompatible and well correlated refractory elements did not fractionate from each other during all lunar differentiation processes leading to the formation of the returned lunar rocks.

It would be unbelievable, if for example the Ba/La-ratio (figure 3) changed during condensation and accretion and then magmatic processes restored the chondritic ratio. In other words, we can be sure that the constant ratio of two correlated elements observed for the limited number of samples collected on the lunar surface is valid for the whole Moon.

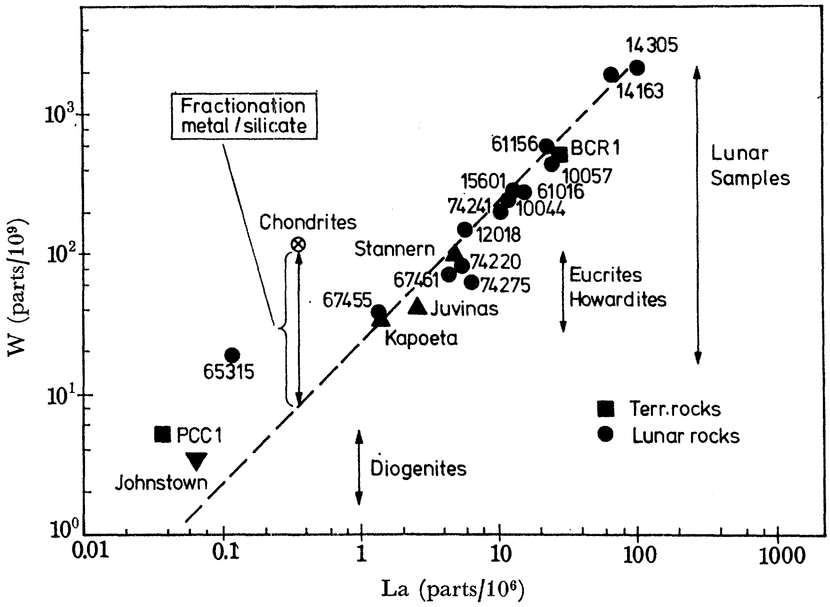

FIGURE 4. W against La. Except for samples with a very low La and W content, an identical ratio is found for lunar and terrestrial samples and for achondrites. Chondrites have a high W/La-ratio indicating metal-silicate fractionation for Earth, Moon and achondrites. All data from this laboratory.

For the pair of moderately volatile elements Rb and Cs we find a similar situation, except it seems that on the Moon the somewhat more volatile Cs is slightly depleted relative to Rb (Wänke *et al.* 1973).

A quite good correlation is observed for the pair W and La (figure 4), but the correlation line of the lunar samples falls about a factor of 17 below the chondritic ratio. The reason for this is the fact that W has a siderophile character. Hence, about 94% of the total W must have been separated with a metal phase and only about 6% went as oxide into the silicates and fractionated together with La. A very surprising observation, however, is the fact that it seems that terrestrial samples have similar W/La-ratios as the lunar samples. The same W/La-ratio is also found in achondrites. The Earth is thought to have about 10 times more metallic iron than the Moon. Hence, the identical W/La-ratio for the Moon and the Earth might have an important bearing on the origin of the Moon (see Dreibus *et al.* 1976, this volume).

Correlations like K/La which has been studied thoroughly by our group are of special significance (figure 5). One of the elements, in this case, K belongs to the group of moderately volatile elements, while La is a refractory element. (Of course, both are l.i.l. elements, i.e. both are large ion lithophile elements.) In such cases, Moon, achondrites, Earth and chondrites plot along separate correlation lines. The Moon being a factor of 30 off the chondritic ratio must have been either enriched in La or depleted in K. As we will see later on, the truth lies in the middle; we find for La an enrichment by a factor of 10 and for K a depletion by a factor of 3. For a further discussion about correlated elements see the paper of Palme & Wänke (1976) in this volume.

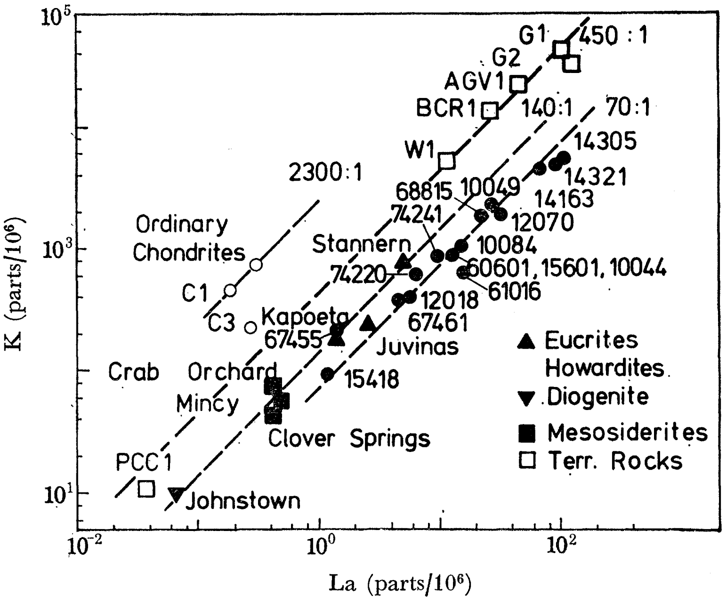

FIGURE 5. K against La in lunar, terrestrial and meteoritic samples.

THE BUILDING BLOCKS OF THE MOON

The Ca, Al-rich Allende inclusions brought the proof that during condensation all the refractory elements stayed together as a group. In a thorough investigation including practically all refractory elements, Wänke *et al.* (1974*b*) found almost identical enrichment factors of these elements in such an inclusion.

Due to their strong group behaviour we can take La as a measure for the refractory elements or the group of high temperature condensates; they represent the refractory portion of the Moon.

For the non-refractory portion (mainly the Mg, Fe-silicates) the situation is a more difficult one. Until very recently, no element was found which belongs to this group and which shows a good correlation with an element of the refractory group and which could therefore be used to estimate the abundance of the Mg, Fe-silicates. As it is discussed in the paper of Dreibus *et al.* (1976) of this conference, Li may be such an element, but up to now we have tried to connect the Mg, Fe-silicates with the moderately volatiles and use K for this purpose, which correlates so nicely with La. We have to admit, however, that it is difficult to estimate with certainty the depletion of K relative to Mg. Our old estimates lead to a 50:50 ratio of the refractory to non-refractory portion of the Moon. Furthermore, the Mg/Fe-ratio can also only crudely be estimated. The first break-through in this respect – as we think – was the discovery of primary matter in the lunar highlands (Wänke *et al.* 1974*a*, 1975).

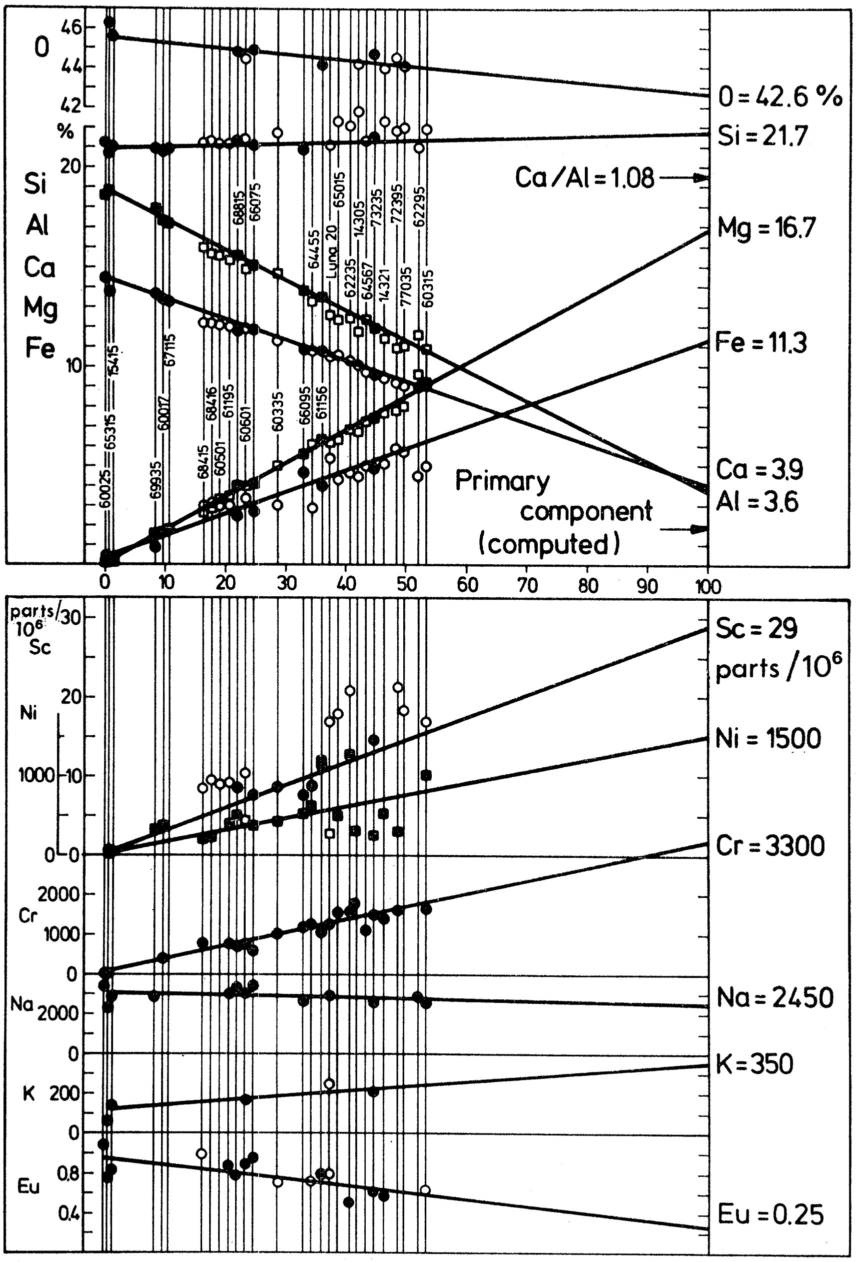

FIGURE 6. Mixing diagram for lunar highland samples taken from Wänke *et al.* (1975), where references can be found. The sample positions along the *x*-axis were calculated from the data of Al, Ca and Mg alone, without any assumption about possible end-members. The left hand end-member is clearly represented by the lunar anorthosites. The metal-free composition of the primary component as second end-member was calculated assuming a chondritic Ca/Al-ratio of 1.08 for this component.

Primary matter in the lunar highlands

According to our interpretation most of the lunar highland samples represent mechanical mixtures – at least as far as their chemistry is concerned – of three major components:

(1) The lunar anorthosites which are cumulates of a fractional crystallization process of the outer regions of the Moon.

(2) KREEP, representing the first liquid of a partial melting process from the deep interior of the Moon; it was never observed in pure form.

(3) A Mg-rich primary component representing the material of the last accumulation stage of the Moon which was added after a solid feldspathic crust had already formed.

Subtracting KREEP the contribution of which is not significant for the major elements, practically all highland samples fit exactly in a two component mixing diagram (figure 6). This diagram contains samples from Apollo 14, 16 and 17 and also Luna 20.

Table 1. Composition of primary component as observed in the lunar highlands

element	composition computed	refractory portion	non-refrac. portion	non-refrac. portion 100%	C1
O %	41.4	9.0	32.4	40.4	47.0
Si	21.1	2.9	18.2	22.7	10.8
Mg	16.4	1.3	15.1	18.8	9.25
Fe (FeO)	11.0	—	11.0	13.7	17.8
Ca	3.8	3.8	—	—	0.91
Al	3.5	3.5	—	—	0.84
Ti	$\leqslant$ 0.41	$\leqslant$ 0.41	—	—	0.041
Cr	0.32	—	0.32	0.40	0.23
Na	0.24	—	0.24	0.30	0.48
Mn	0.15	—	0.15	0.19	0.17
Fe (metal)	2.4	—	2.4	3.0	—
Ni	0.15	—	0.15	0.19	0.98
S	0.30	—	0.30	0.37	5.9
K (parts/10^6)	(~ 340)	—	(~ 340)	(~ 425)	480.0
Sc	28.0	28.0	—	—	5.2
Eu	0.25	0.25	—	—	0.05
Al/Sc	—	1250	—	—	1610
Al/Eu	—	140000	—	—	168000
Mg/Cr	—	—	—	47	40
Na/Mn	—	—	—	1.6	2.8
Na/K	—	—	—	~ 7	10

Contrary to the general approach this mixing diagram was computed by using the data of the composition of the mixtures only, without any assumption whatsoever about the end-members. The end-member of the left hand side is certainly to be found in the lunar anorthosites. The other must, according to our interpretation, be found at the location where the Ca/Al-ratio approaches the chondritic value of 1.08.

For the bulk Moon we calculated for the refractory portion an abundance of 50 %. In the primary matter of the lunar highlands we find only 21 % refractories, indicating an inhomogeneous accretion of the Moon starting out with a refractory core and more and more non-refractory material added until the Moon reached its final mass. In spite of the change of the ratio of refractories to non-refractories we can quite safely assume that the composition of the non-refractory component did not change significantly during the accretion process of the Moon. Especially we can assume that the ratio MgO/FeO remained unchanged.

Bulk composition of the Moon

In table 1 we have put together the computed composition of the primary component as recognized in the lunar highlands. We observe approximate chondritic element ratios for the refractory and non-refractory portion, except that the moderately volatile elements Mn and Na are depleted by about a factor of 3 relative to Mg, if compared with C1 abundances. The directly obtained concentration for K is of no significance, because in this case the error may be as high as a factor of 2 due to its high abundance in KREEP. Assuming the same depletion factor for K as for Na and assuming that the K/Mg-ratio remained unchanged during the accretion of the Moon, we can use K as a measure for the abundance of the non-refractory portion of the Moon and find with Mg = 9.25 % and K = 480 parts/10^6 for C1 chondrites a K content of the non-refractory portion of 325 parts /10^6.

With the relation

$$\left(\frac{\mathrm{K}}{\mathrm{La}}\right)_{\mathrm{Moon}} = \frac{(1-x)\,[\mathrm{K}]}{x\,[\mathrm{La}]}$$

$$x = \text{refr. portion}$$

$$(1-x) = \text{non-refr. portion}$$

and with a lunar K/La-ratio of 70 and a La concentration of the refractory portion of 4.9 parts/10^6 as measured in an Allende inclusion (Wänke *et al.* 1974*b*), we calculate a 50:50 ratio for the refractory to the non-refractory portion of the Moon. The resulting mean bulk composition of the Moon is summarized in table 2. Another approach to estimate the bulk composition of the Moon was made by Ganapathy & Anders (1974). Their estimate is based in part on quite different constraints, but also involves grouping of elements in the condensation sequence. They arrive at somewhat lower concentrations of refractory elements.

Table 2. The bulk composition of the Moon as derived from the calculated 50:50 ratio of the refractory and non-refractory portion

element	refractory portion	non-refractory portion	Moon	element	refractory portion	non-refractory portion	Moon
O %	21.8	20.2	42.0	K (parts/10^6)	—	(175)	175
Si	7.0	11.4	18.4	Rb	—	(0.4)	0.4
Mg	3.2	9.4	12.6	Cs	—	(0.02)	0.02
Fe (FeO)	—	6.9	6.9	Sr	65	—	65
Al	8.5	—	8.5	Ba	24	—	24
Ca	9.0	—	9.0	Sc	60	—	60
Ti	0.46	—	0.46	Y	17	—	17
Na	—	0.15	0.15	La	2.5	—	2.5
Cr	—	0.20	0.20	Eu	0.57	—	0.57
Mn	—	0.09	0.09	Zr	47	—	47
Fe (metal)	—	1.5	1.5	V	310	—	310
Ni	—	0.09	0.09	Nb	3.3	—	3.3
S	—	0.19	0.19	Ta	0.13	—	0.13
				Th	0.22	—	0.22
				U	0.06	—	0.06

Finally, we like to emphasize two points:

(1) We are not proposing the Ca, Al-rich Allende inclusions to be part of the building blocks of the Moon, but only take the observed elemental abundances of these inclusions as experimental values for the condensation sequence. The difference of the oxygen isotope ratios of Allende inclusions and the Moon clearly excludes a direct connection (Clayton *et al.* 1973). The condensation sequence, however, did probably not differ too much at different locations of the solar system as far as the refractory elements are concerned.

(2) This is a purely compositional model of the Moon calculated from observed element ratios of correlated elements. It is based exclusively on geochemical grounds. Nothing is said and no assumptions were made about how this composition was achieved or about the physical origin of the Moon.

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