NON-METEORITIC SIDEROPHILE ELEMENTS IN LUNAR HIGHLAND ROCKS:
EVIDENCE FROM PRISTINE ROCKS.

H. Wänke, Gerlind Dreibus, and H. Palme
Max-Planck-Institut für Chemie (Otto-Hahn-Institut), 65 Mainz, F. R. Germany

Large amounts of siderophile elements are found in lunar highland breccias especially in those of the Apollo 16 mission. Nickel concentrations sometimes exceed 1000 ppm. Today the siderophile elements reside almost exclusively in small metal grains. According to a widespread prejudice, the meteoritic origin of a metal phase is thought to be proven if the Ni/Co ratio is close to the chondritic value of 21. However, in the earth's mantle Ni and Co are present in oxidized form in almost exactly this ratio. Any reduction process on such mantle material would generate a metal undistinguishable from meteoritic metal with respect to the Ni/Co ratio. The observation that in the lunar highland breccias Ni and Co as well as other siderophiles - including W, which is certainly of lunar and not of meteoritic origin - are contained in metal grains does not preclude the possibility that a considerable portion of Ni and Co was originally present in oxidized form in the silicates. In fact, the redistribution of certain elements between metal and silicates in lunar samples has been recognized by various authors (1-3).

In our contribution to the last LPSC (4) we have shown that large portions of Ni and Co found in lunar highland breccias are non-meteoritic in origin but indigenous to the lunar primary matter. Using different arguments Delano and Ringwood (5) reached similar conclusions. This point of view was strongly opposed by Anders (6) who favored an almost exclusively meteoritic origin of these elements.

In this controversy the so-called "pristine highland rocks" were used as a major evidence for a very low indigenous Ni content of lunar highland rocks. In fact we now think that "pristine non-mare rocks" as recognized and thoroughly analyzed by Warren and Wasson (7) represent "keystones" for the understanding of the siderophile elements in lunar highland rocks. The arguments based on the chemistry of pristine rocks are straightforward.

If the moon was formed from the earth's mantle after core formation as it has been advocated by various authors (8-14) or if it was formed in some other way from material chemically similar to that of the earth's mantle, high concentrations of Ni and Co are expected in the bulk moon. The magma ocean from which the lunar crust may have differentiated should then have contained some 2000 ppm Ni and 100 ppm Co. Obviously we cannot expect to find such high concentrations of Ni in any igneous lunar rock. The presence of small amounts of metallic iron either indigenous or of meteoritic origin or formed by in situ reduction would lead to the extraction of most of the Ni and of a considerable portion of Co. Crystallization of olivine would further reduce the Ni content of the magma due to the large olivine-liquid partition coefficient of Ni. However, Co will be significantly less affected because of its smaller partition coefficients (metal-silicate and olivine-liquid). In pristine non-mare rocks Warren and Wasson (7) found indeed Co concentrations up to 30 to 50 ppm.

The Co/Fe+Mg ratio stays constant for all pristine non-mare rocks (Fig.1). Siderophile-rich highland breccias have much higher Co/Fe+Mg ratios because of the obvious addition of Co from meteoritic sources. If we now for the moment assume all Ni to be of exclusively meteoritic origin and correct the observed Co concentrations in highland breccias for meteoritic contribution, using Ni as a monitor for this contribution and assuming a chondritic Ni/Co ratio, we find that the data points corrected in this way fall below the correlation line of the pristine rocks (Fig.2). Subtraction of a meteoritic component from highland breccias, based on Ni and on a chondritic Ni/Co ratio would require a class of...
NON-METEORITIC SIDEROPHILE ELEMENTS

H. Wänke et al.

highland rocks with much lower Co concentrations than those found in pristine highland rocks (Fig. 2). Since this result is clearly unreasonable, we have subtracted a meteoritic component based on Ir and a chondritic Ir/Co ratio. The result of this approach can be seen in Fig. 3. Now the data points from pristine rocks and those of siderophile-rich highland breccias almost overlap. We conclude that large amounts of Ni present in the highland breccias are of non-meteoritic origin. The only alternative would be to assume a population of impacting bodies with non-chondritic and variable Ni/Co ratios. In view of the extreme constancy of the Ni/Co ratio in all chondrite classes, we can according to Ockham's Razor completely exclude this possibility.

The constancy of the Co/Fe+Mg ratio observed for the pristine highland rocks even extends to lunar mare basalts. As we can see from Fig. 4 the low Ti mare basalts plot along the correlation line of the pristine highland rocks. Terrestrial basalts and primitive peridotitic nodules which represent almost unfractonated material of the earth's upper mantle have higher Co/Fe+Mg ratios. However, we have to keep in mind that lunar Co concentrations were probably lowered due to the segregation of small amounts of metal. Even siderophile-rich highland breccias contain in part material which was subjected to such a depletion of Ni and Co.

High indigenous Ni and Co concentrations in lunar highland rocks, fit well into the model of Wänke et al. (4,15-17), who have repeatedly advocated the existence of an unfractonated (primary) component in lunar highland rocks. According to this model highland breccias are mechanical mixtures of materials from quite different sources. Neglecting material added by meteoritic impacts...
and that from trace element-rich (highly advanced) KREEP liquids, we are left with only two major components which significantly contribute to the major element chemistry, i.e. a feldspathic (lunar anorthosites) and a mafic (Mg-rich) component. The Mg-rich component (MgC) itself was found to consist of two components, i.e. 41% of material derived from (less advanced) residual liquids (RL) from which olivine and plagioclase have separated and 59% of nearly unfractonated primary matter (PC), which was either added to the moon only after a solid feldspathic crust had already been formed or which in some other way has escaped large scale fractionations. Thus, the relative abundance of the mafic non-meteoritic elements of the highland breccias should come close to that in the MgC. In Table 1 we have listed the major element compositions of MgC, RL and PC as taken, respectively derived, from the data given by Wänke et al. (17).

We realize from Fig. 3 that the siderophile-rich highland breccias have slightly higher Co/Fe+Mg ratios than pristine highland rocks, i.e. 2.48 x 10^{-4}, resp. 1.81 x 10^{-4}. Wänke et al. (4) obtained for the highland breccias after (Ir) correction for the meteoritic contribution a Ni/Mg ratio of 6.3 x 10^{-5} which leads for the MgC to an absolute concentration of 1000 ppm Ni. As stated above the contribution from material from RL will be small in the case of Ni. Assuming a RL concentration of 100 ppm Ni we obtain for the PC a value of 1600 ppm Ni.

For Co the contribution from RL is more significant, but can be directly inferred from the observed Co/Fe+Mg in the pristine highland rocks. With the value of this ratio of 1.81 x 10^{-4} we find for RL a value of 40 ppm Co. With the Co/Fe+Mg ratio of 2.48 x 10^{-4} for highland breccias we get for MgC a value of 64 ppm Co which finally yields for PC a value of 80 ppm Co. These values for Ni (1600 ppm) and Co (80 ppm) are slightly lower than our previous estimates, but the Ni/Co ratio and the Mg/Ni ratio match now almost exactly that of the earth's mantle and the absolute concentrations are still in good agreement (earth's upper mantle: 2000 ppm Ni, 100 ppm Co, and 22.5% Mg; see Jagoutz et al. (18)).

The high concentrations of Ni and Co in the earth's mantle are not yet fully understood, they are a very special feature of the earth as it is also underlined by the low concentrations of these elements in the EPB (Fig. 4). Thus the genetic relationship of earth and moon is further stressed.