HIGHLY SIDEROPHILE ELEMENT ABUNDANCES IN LUNAR IMPACT ROCKS AND IMPLICATIONS FOR THE VOLATILE BUDGET OF THE SILICATE EARTH.

H. Becker[1] and M. Fischer-Gödde[1,2], [1]Institut für Geologische Wissenschaften, Freie Universität Berlin, Malteserstrasse 74-100, D-12249 Berlin, Germany (hbecker@zedat.fu-berlin.de), [2]Institut für Planetologie, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Str. 10, D-48149 Münster, Germany.

Introduction: The origin and timing of accretion of water and other highly volatile elements in the terrestrial planets remains debated, some arguing for accretion during the main stages of planet building [1], whereas others favor supply by a late veneer after core formation as the dominant process [e. g., 2, 3].

It has been noted that the abundances of H, C, N and S and the highly siderophile elements (HSE) in the silicate part of the terrestrial planets may share a common history [e. g., 2]. Abundances of HSE in ancient lunar impact rocks provide insight into the history of late accretion of meteoroids [e. g., 4], and may thus also yield clues to better understand the origin of highly volatile elements in the Silicate Earth. Differences in HSE abundance ratios in different chondrite groups and metal rich differentiated meteoroids [e. g., 4-8] form the basis to distinguish different types of impactor compositions. Here we explore, using recent HSE abundance and ^{187}Os/^{188}Os data of lunar impact rocks and terrestrial samples, the role of carbonaceous chondrite like materials for the budget of H, C, N and S in the Silicate Earth.

HSE Abundances in Ancient Lunar Impact Rocks: Early work on abundances of Ir, Au and Re in pre-3.8 Ga lunar impact melt rocks and breccias has identified several compositional groups that may be tied to specific basin-forming impactors [4-5]. More recently, improved analytical techniques and the application of the Re-Os system have led to further characterization of the HSE compositions of ancient lunar impactors and the mixing relationships with each other or with ancient highland crust [9-12]. The recent work, summarized in Fig. 1, has indicated the presence of enstatite or ordinary chondrite like compositions (Apollo 17 aphanites), compositions that tend to have slightly suprachondritic ^{187}Os/^{188}Os, Ru/Ir and Pd/Ir (Apollo 17 poikilitic impact melt rocks [9,10]), and a component with suprachondritic HSE compositions that are similar to compositions of some Group IVA iron meteorites [5,11]. Lunar granulites display CI and CM chondrite like ratios of volatile and moderately volatile elements but variable depletion of these elements, which has been attributed to partial volatile loss during impact processes [5, 11, 13]. Lunar granulites occur at Apollo 16 and 17 landing sites and may represent highland rocks thermally annealed by impact melt sheets or recrystallized impact melt rocks [14].

HSE Systematics of Earth's Primitive Mantle: Refinement of the HSE composition of the Earth's primitive mantle (PM) is based on improved analytical techniques for the determination of HSE concentrations in terrestrial peridotites [e. g., 15,16], and corroborated by ^{187}Re-^{187}Os and ^{190}Pt-^{186}Os isotope data [17, 18]. According to this data, PM is characterized by chondritic ratios of HSE, with the exception of ratios involving Ru and Pd, which are 20-30 % higher than in chondrites. Moreover, it has been noted that specific ratios, such as Re/Os and Rh/Ir, are higher than values from carbonaceous chondrites [15-17]. These deviations may reflect late accretion of either i) primitive materials with slightly suprachondritic ratios of some HSE, ii) mixtures of chondritic materials with differentiated suprachondritic late veneer components, or iii) a late veneer mixed into terrestrial mantle with a fractionated HSE component left behind after core formation [9-11,15-20].
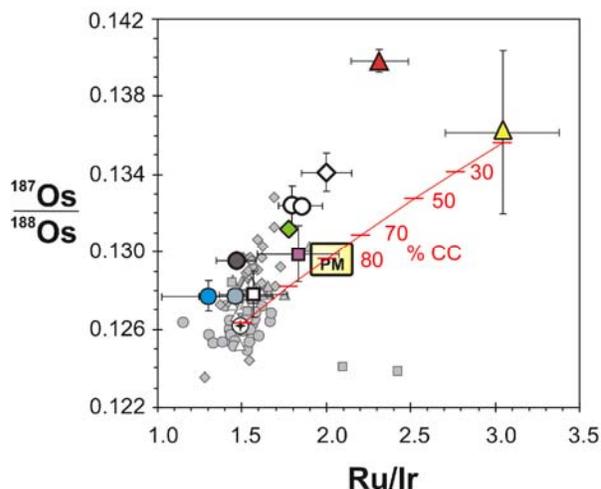

Fig. 1. Meteoritic end member compositions obtained from ancient lunar impact rocks in comparison to compositions of chondrites (small gray symbols, [6-8]). Open circles and diamonds: Apollo 17 poikilitic melt rocks, dark gray circle: Apollo 17 aphanites, blue circles: lunar granulites, triangles: Apollo 16 impact melt rocks, green diamond: Apollo 15 impact melt rock, open and purple squares: lunar meteorites, circle with cross: CI chondrites. Earth's Primitive Mantle (PM) from [15].

Matching Lunar Impactor Compositions and the HSE Composition of the Silicate Earth: The proximity of Earth and Moon suggests that both bodies may have accreted similar materials between 4.5 and 3.8 Ga, although the mass accretion rate at a given time must have been different [21]. Specific HSE ratios in fertile lherzolites from the Earth's mantle are either constant (in particular Ru/Ir) or converge towards specific compositions (e. g., $^{187}Os/^{188}Os$ [15, 17]). Additional constraints from komatiites [e. g., 22] tend to support inferences from peridotites. This behavior is expected if most of the Earth's mantle has been well-stirred over the past 3 Ga. If the HSE composition of Earth's PM solely reflects contributions from a late veneer, this composition can be explained by predominance of two components: about 75-85 % of a chondritic composition, best matched by a slightly volatile depleted carbonaceous chondrite composition (gray circles in Fig. 1), and 25-15 % of a fractionated component with HSE characteristics similar to some IVA iron meteorites (e. g., Fig. 1, and similar diagrams with Pd/Ir or Au/Ir, which are not shown here).

Volatile Supply to the Silicate Earth by Late Accretion: Studies of the abundances and isotopic composition of water, nitrogen and carbon in terrestrial samples and other solar system materials suggest that the most likely origin of these elements in the Earth is by major contributions from carbonaceous chondrite like material supplied in part or completely by late accretion after core formation [e. g., 23]. Late accretion of carbonaceous chondrite material is indicated by CI to CM like ratios of some volatile elements in lunar granulites (e.g., Se/Ag, Zn/Ag, [5,13]), lunar soils [24], and possibly the presence of water in some lunar glasses [25]. Abundances of H_2O, C, N and S in the Earth's primitive mantle can be estimated by assuming that the complete budget of these elements in the latter has been acquired by late accretion [e.g., 21]. The fraction of late accreted material may be calculated from the Ir abundance in PM (0.0080±0.0009*CI chondrites, [15]). The mixing relationship outlined in Fig. 1 is taken as a model to explain the HSE composition of PM by 75-85% carbonaceous chondrite material and 25-15 % degassed and differentiated (IVA iron like) material. Typical abundances of H_2O, C, S and N in CI and CM meteorites [26-27] and suitable iron meteorite compositions yield the following ranges for calculated PM model compositions: 380-930 ppm H_2O, 80-170 ppm C, 6-14 ppm N and 130-270 ppm S. With the exception of N, these values compare well with estimates derived from terrestrial samples [23, 28]. By far the largest uncertainty in these estimates is imposed by the choice of the specific carbonaceous chondrite composition. CI compositions seem to yield a better match with independent estimates for H_2O, C and S in PM than slightly depleted (CM like) carbonaceous chondrite composition (0.5* CI). Calculated N abundances in PM are too high by a factor of 4 to 8, compared to PM estimates based on terrestrial samples. More volatile element depleted carbonaceous chondrite compositions would result in a collateral decrease of abundances of H_2O, C and S in PM. The discrepancy for N indicates that the model of a late veneer of predominantly carbonaceous chondrite like material may be too simple to fit the terrestrial abundance pattern of H, C, S and N. The discrepancy may be resolved in various ways: i) Accretion of primitive materials with higher C/N and H/N than carbonaceous chondrites (comets? [29]). ii) Preferred loss of N during accretion of impacting bolides. iii) Larger fractions of H, C and S (but not N) in PM may have been retained from the pre-4.5 Ga growth period of the planet, and late accretion has added only a minor fraction of these elements.

References: [1] Abe, Y. et al. (2000) in *Origin of the Earth and Moon (ed. Righter, K. & Canup, R.M.),* 413-433. [2] Drake, M.J. and Righter, K. (2002) *Nature., 416,* 39-44. [3] Albarede, F. (2009) *Nature 461,* 1227-1233. [4] Morgan, J. W. et al. (1974) *Proc. Lunar Sci. Conf.* 5, 1703-1737. [5] Hertogen, J. et al. (1977) *Proc. Lunar Sci. Conf.* 8, 17-45. [6] Horan, M. F., et al. (2003) *Chem. Geol.*, *196*, 5-20. [7] Brandon, A.D. et al. (2005) *GCA, 69,* 1619-1631. [8] Fischer-Gödde et al. (2010) *GCA, 74,* 356-379. [9] Norman et al., 2002, *EPSL*, 202, 217-228. [10] Puchtel et al. (2008), *GCA*, 72, 3022-3042. [11] Fischer-Gödde et al. (2010), *Lunar Planet. Sci. XLI*, Abstract 2262. [12] Day et al. (2010), *EPSL, 289*, 595-605. [13] Higuchi, H. & Morgan, J. W. (1975) Proc. 6th Lunar Sci. Conf., 1625-1651. [14] Norman, M.D. et al. (2007) *Lunar Planet. Sci. XXXVIII*, Abstract 1991. [15] Becker, H. et al. (2006) *GCA*, *70*, 4528-4550. [16] Fischer-Gödde, M. et al. (2011) *Chem. Geol.*, in press. [17] Meisel, T. et al. (2001) *GCA, 65,* 1311-1323. [18] Brandon A. D. et al. (2006) GCA 70, 2093- [19] Dauphas, N. et al. (2002) *Geochem. J., 36* 409-419. [20] Walker, R. J. (2009) *Chem. Erde, 69*, 101-125. [21] Chyba, C.F. (1991) *Icarus, 92,* 217-233. [22] Puchtel, I. S. et al. (2009) *GCA, 73* 6367–6389. [23] Marty, B. & Yokochi, R. (2006) *Rev. Min. Geochem., 62*, 421-450. [24] Keays, R. R. et al. (1970) *Science 167*, 490-493. [25] Saal, A. et al. (2008) *Nature 454*, 192-195. [26] Kerridge, J.F. (1985) *GCA, 49,* 1701-1714. [27] Pearson, V. et al. (2006) *Met. Planet. Sci., 41*, 1899-1919. [28] Lorand, J.-P. (1990) *GCA, 54,* 1487-1493. [29] Dauphas, N. (2003) Icarus, 165, 326-339.