HIGH U-PB RATIOS IN THE SOURCE OF LOW-TI VOLCANIC GLASS BEADS FROM THE APOLLO 14 SOIL.

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Introduction: Lead isotope geochemistry is a powerful tool used in the variety of geochemical studies. The basis for terrestrial application of isotope systematics of lead (Pb) was established almost 40 years ago by pioneering work that determined evolution of Pb isotope compositions in the major terrestrial reservoirs [e.g. 1, 2]. However, the study of Pb systematics of lunar samples was hindered by a combination of low Pb abundance, very radiogenic nature of lunar Pb, common disturbance of U-Pb system by impacts and terrestrial contamination [e.g. 3-5]. Nevertheless, initial analytical results obtained from lunar samples, including mare basalts, indicated relatively high ($\sim$100-600) $^{238}U/^{204}Pb$ ratios (or μ-values) to be characteristic of the sources of lunar rocks. Comparison of lunar Pb systematics with terrestrial silicate rocks showing μ-values of about 8-10 suggests that the Pb depletion observed on the Moon cannot be explained by fractionation of silicate melts or segregation of sulphides and therefore must be determined by a very early volatile loss of Pb from the Moon. The early work also showed that some volcanic glasses preserved as sub millimeter size spheres in the lunar soils indicate relatively low μ-values in their source [5, 6] The apparent difference between Pb systematics of mare basalts and volcanic glass beads was interpreted as indicative of different sources, relatively primitive (low-μ) for magmas forming glass beads and relatively evolved (high-μ) for the mare basalt magmas [5]. However, analysis of U-Pb systematics in several lunar meteorites [e.g. 7-9] suggests a possibility of existence of basalts with the low μ-values in their sources. In addition, a relatively small number of glass beads has been analysed, compared to the number of mare basalts, inhibiting the ability to make firm conclusions regarding the differences or similarities of their sources. In this study we have analysed green glass beads extracted from the Apollo 14 soil sample 14163 to investigate further the proposed difference in the μ-values defined by the volcanic glass beads and mare basalts.

Results: U-Pb data were collected using the Cameca ims1270 ion probe in Stockholm. Single analysis consisted of 30 blocks where Pb isotopes have been measured simultaneously on the muticollector

system followed by the sequence of measurements of ^{238}U, $^{232}Th^{16}O$ and $^{238}U^{16}O$ using one of the collectors. Collector efficiencies have been cross calibrated using BCR-2 glass inserted into the mount containing glass beads. The same glass was used to correct for elemental fractionation and determine true values for U-Pb and Th-U ratios in the lunar volcanic glasses.

Although ion probe data are less precise than those obtained by other analytical methods, such as Thermal Ionisation Mass Spectrometry (TIMS), and require a standard to determine true value for U-Pb ratio, they allow investigation of very small sample spot (10-20 μm) on the surface of a polished mount or thin section and so can address the issue of small scale homogeneity of the samples. Applied to the studies of glass beads, SIMS permits several analyses in a single sub-millimeter size bead. Consequently individual beads with a known origin can be analysed and preserved for further studies. In addition, the ion probe data do not require complex chemical preparation of samples and therefore are less influenced by terrestrial contamination.

Glass beads extracted from lunar soils commonly represent mixtures of pristine glasses of volcanic origin and impact generated glasses. Previous work determined criteria for identification of pristine volcanic beads [10]. Following this criteria initial selection of about two hundred glass spherules extracted from Apollo 14 soil sample 14163 and ranging in colour from green to yellow, orange, red and black were checked for homogeneity using back scattered electron imaging, as the impact-related glass beads often show schlieren as well as mineral and lithic inclusions, inherited from their formation at lower temperature [10]. Further selection was based on the chemical composition of homogenous beads. The analyses of mare soils, impact and volcanic glasses [10] show that volcanic glasses have Mg/Al ratio higher than 1.5. Application of this limit to the beads extracted from the sample 14163 resulted in identification of 27 volcanic spherules. Seven of these beads showed very low Pb concentration. All remaining beads are green in colour, show low-Ti content (<1.3 wt % of TiO_2) and can be further subdivided into three groups Green A, VLT (very low Ti) and Green B defined by other studies [e.g. 10]. Chemical variations observed in the beads

from sample 14163 are consistent with the previous studies describing these three types of pristine volcanic glasses [10, 11]. The Green A spherules show distinct chemical difference from other two groups (e.g. significantly lower #Mg and higher Ti/Al), whereas VLT and Green B glasses partially overlap, although the latter show generally higher #Mg value, Ti, Fe and Mg content and lower Al, Ca, Na and K content. In addition, Green B and VLT beads can be unambiguously separated by substantial differences in their U-Pb systematics.

Initial Pb uncorrected U-Pb analyses of all beads appear to be concordant, although the concordance in this case is misleading as the trend towards the possible radiogenic initial Pb compositions is almost parallel to the concordia curve. As a result any correction for radiogenic initial Pb will result in the shift of analytical points towards younger ages, but without visible change in concordance. Constraining linear fits through analytical points uncorrected for the initial Pb using either $^{238}U/^{206}Pb$-$^{207}Pb/^{206}Pb$-$^{204}Pb/^{206}Pb$ or $^{204}Pb/^{206}Pb$-$^{207}Pb/^{206}Pb$ systematics helps to avoid problem of undefined initial Pb composition. The approach relies, however, on the assumption that all analysed samples are of the same age and originate from the same source so that the identified liner trends are determined by the mixing of Pb accumulated in the samples as a result of U decay and the initial lunar Pb inherited from the source of the melt that formed collected glass beads. Distribution of analyses on the $^{207}Pb/^{206}Pb$ vs. $^{204}Pb/^{206}Pb$ diagram indicates that Green A and VLT glasses can be considered to originate from the sources with similar (within error), relatively radiogenic isotope compositions of Pb, whereas Green B beads represent melts that derived from distinctly different less radiogenic source. A similar difference is observed in the $^{208}Pb/^{206}Pb$ vs. $^{204}Pb/^{206}Pb$ diagram. Best fit lines based on the analyses of Green B and combined Green A and VLT glasses define ages in $^{238}U/^{206}Pb$-$^{207}Pb/^{206}Pb$-$^{204}Pb/^{206}Pb$ and $^{204}Pb/^{206}Pb$-$^{207}Pb/^{206}Pb$ systems that are similar within the errors. The ages determined for both groups are in the range of 3.2-3.3 Ga similar to that determined from the earlier TIMS analyses of bulk samples of green glasses and many mare basalts [3, 4, 6]. However, $^{238}U/^{206}Pb$ determined by ion probe require correction using a standard with known U-Pb ratio, which introduces an additional source of uncertainty. Consequently, $^{207}Pb/^{206}Pb$-$^{204}Pb/^{206}Pb$ systematics was used to calculate µvalues for the sources of studied glass beads.

The presence of at least two (more and less radiogenic) sources in the lunar mantle indicated by the analysed green glass beads from the Apollo 14 soil confirms the observation that chemical variations between the Green A, Green B and VLT glass beads cannot be explained by the fractionation of a melt derived from the same mantle source [e.g. 11]. These chemical variations are interpreted in terms of a fractionation-assimilation model [11] suggesting various proportions of mixing between more primitive mantle melts and the KREEP (high K, REE and P) component during the accent of basaltic magma or variable mixing of KREEP material into the mantle as a result of a mantle overturn that followed solidification of the Lunar Magma Ocean. Correlation between chemistry and Pb isotope systematics in the studied glass beads indicates that the isotopic difference can be also explained by different proportion of KREEP contribution in the basaltic melt. The most K-rich Green A and VLT glasses trend towards the most radiogenic initial Pb, while generally low-K Green B glasses trend towards a less radiogenic source. Green A and VLT glasses with intermediate K-content also indicate a moderately radiogenic source. Considering this interpretation and likelihood that a mantle source represents a range of chemical and isotopic compositions rather than unique concentrations and isotopic ratios, limits of U-Pb ratios (i.e. µ-values) can be calculated for the sources of Green A and VLT melts and Green B glasses as 542±132 and 224±180 (the errors represent maximum limits and are determined by propagating all analytical uncertainties and uncertainties in all mode parameters used in the calculations, such as time of differentiation of lunar mantle and the initial lunar Pb prior to differentiation).

The results indicate a high-µsource for the Apollo 14 green beads magmas, suggesting that there is no difference in the range of µ-values between the sources of volcanic glasses and mare basalts. The variation of µ-values can be explained by a different proportion of mixing between a relatively primitive source and KREEP, although the mechanism of this mixing cannot be determined based solely on the U-Pb systematics of lunar samples.

References: [1] Stacey and Kramers (1975) *EPSL, 26*, 207-221. [2] Zartman and Doe (1981) *Tectonophysics, 75*, 135-162. [3] Tera and Wasserburg (1974), *Geochim.Cosmochim.Acta, 2*, 1571-1599. [4] Tatsumoto, (1970), *Science, 167*, 461-463. [5] Tatsumoto et al. (1987), *JGR, 92,* 361-371. [6] Meyer et al. (1975), *Proc. 6th LSC*, 1673-1699. [7] Misawa et al. (1993), *Geochim.Cosmochim.Acta, 57*, 4687-4702. [8] Kita et al. (1995), *Geochim.Cosmochim.Acta, 59* 2621-2632. [9] Terada et al. (2008), *EPSL, 270*, 119-124. [10] Delano (1986), *JGR, 91*, 201-213. [11] Schearer et al., 1990 *Geochim.Cosmochim.Acta, 54* 851-867.