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## Quantitative Evolved Gas Analysis of Apollo Lunar Soils

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**Introduction:** Recently we have developed a quantitative evolved gas analysis (QEGA) method for geological samples [1]. It is based on calibration of the registration device, a quadrupole mass spectrometer (QMS), by passing through it reference gases with known flow rates. For calibration purposes we used pure gases such as H<sub>2</sub>, He, N<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub> and Ar as well as mixtures thereof. The method was first tested using compounds such as CaCO<sub>3</sub>, CaC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O, PdO, NaHCO<sub>3</sub> that give known amounts of simple gases upon their thermal decomposition. A precision of about 20% (1σ) was achieved for the absolute amounts of the analysed gases. The method was then applied for the analysis of meteorite reference samples, Murchison and Allende [2]. In the present study we applied the QEGA method to five Apollo lunar soil samples that have been previously analysed for C, N and noble gases using stepped combustion [3].

**Samples:** The samples analysed include soils collected by Apollo 12, 14, 15, 16 and 17 missions (12070, 14141, 15040, 69921 and 72501 respectively), representing a range of maturity from extremely mature, 15040 (I<sub>s</sub>/FeO=94) to immature, 14141 (I<sub>s</sub>/FeO=5.7) [3].

**Experimental:** Adapting the experimental protocol described in [1] the flow rate of reference gases was regulated with three standard (1/32 inch) capillary pipes with crimps instead of PZT valve. Each capillary is set to provide a fixed flow rate. Pneumatic valves enable the gas flow to be switched between individual or combinations of capillaries such that five different fixed gas flow rates are possible in a range over one order of magnitude. To calibrate the system for water and sulphur dioxide we used decomposition of gypsum. In all experiments the linear heating rate of 12°C/min was applied over the range from 100 to 1400 °C.

**Results:** Typical release patterns of the major gas species from the studied lunar soils are shown in Figures 1 and 2. Most of the released components can be clearly identified. However, the QMS has insufficient resolving power to separate N<sub>2</sub><sup>+</sup> and CO<sup>+</sup> hence the signal at m/z 28 can in principle be a mixture of signals from nitrogen, carbon monoxide and second order signal from carbon dioxide. Analysis of the second order signals from N<sub>2</sub> and CO at m/z 14 and 12 respectively can help to identify the gases contributing to the m/z 28 signal. The relationships between the main and the second order signals have been obtained from the analysis of pure gases. Similarity of signals at m/z 12 and 14 (Figs. 1 and 2)

clearly indicates that at m/z 28 both N<sub>2</sub> and CO make a significant contribution. There are two peaks of N<sub>2</sub>+CO release with the higher intensity observed at lower temperature (also apparent on pressure graph).

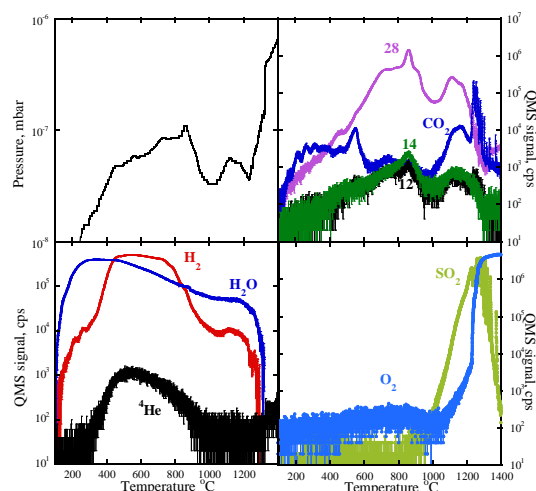


Figure 1. Release patterns of different gases during EGA of mature sample 69921. Pressure variations are also shown.

Release of H<sub>2</sub> basically coincides with that of <sup>4</sup>He. CO<sub>2</sub> appears in two temperature ranges: 200-600 °C and 1000-1300 °C. Water has a broad release pattern almost over the entire temperature range (Fig. 1). SO<sub>2</sub> is released at higher temperature (>1000 °C). There is also a major oxygen release at T >1200 °C associated with the highest record of pressure (Figs. 1 and 2).

**Discussion: Release patterns.** In general, the observed release pattern of different gases corresponds well with those from previously analysed lunar soils using similar (but non-quantitative) method about 50 years ago [3] in which, however, 50-100 times larger sample aliquots than in the present study were used. It includes the double peak of N<sub>2</sub>+CO, the low temperature and simultaneous release of H<sub>2</sub> and <sup>4</sup>He, the high-temperature release of SO<sub>2</sub>, the low- and high-temperature release of CO<sub>2</sub> and the high-temperature release of O<sub>2</sub>. The interpretation of different gas releases associated with certain temperature intervals given in [4] seems reasonable. It concerns the release of solar H<sub>2</sub> and <sup>4</sup>He, the low-temperature release of CO<sub>2</sub> as a result of decrepitation of vesicles or voids and the chemical reactions between different minerals resulting in release of SO<sub>2</sub> from troilite due to its reaction with silicates, and CO due to FeO+C reaction. However, for the appearance of large amounts of O<sub>2</sub> at the very high temperature we suggest that

SiO<sub>2</sub> vapours (from the quartz extraction tube) may be decomposed by the catalytic action of Pt (used to wrap the samples). Gibson and Johnson [3] suggested that in their all-metal extraction system this O<sub>2</sub> was produced as a result of chemical reaction between FeO and the Pt crucible. We cannot exclude that this process is also taking place in our case but its contribution to the O<sub>2</sub> release budget is small since similar O<sub>2</sub> release is also observed in the blank experiments.

The double peak release of solar and non-solar N<sub>2</sub> from lunar soils is observed in experiments of stepped combustion [2, 5] that seems to be related to the lunar soil's maturity. The immature soil 14141 shows only one peak of N<sub>2</sub> release (Fig 2).

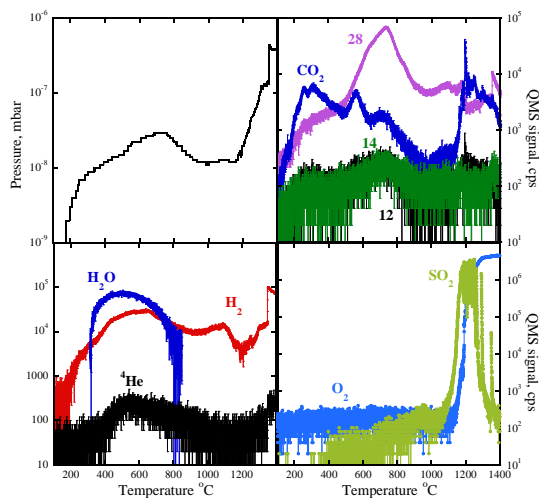


Figure 2. Release patterns of different gases during EGA of immature sample 14141. Pressure variations are also shown.

### Concentrations.

1. Hydrogen. The hydrogen concentrations determined in the samples analysed are (in ppm): 14141 – 32, 15040 – 66, 69921 – 61, 12070 – 36 and 72501 – 64. These concentrations are well within the range (27-70 ppm) determined by a combination of pyrolysis with gas chromatographic methods for Apollo lunar soils [6]. Simultaneous release of <sup>4</sup>He and H<sub>2</sub> suggests that most of this hydrogen appears to be associated with solar wind implantation.

2. Helium. The <sup>4</sup>He concentrations calculated for the samples are (in cc/g): 14141 – 0.014 (0.019), 15040 – 0.085 (0.048), 69921 – 0.046 (0.031), 12070 – 0.072 (0.05-0.06) and 72501 - 0.22 (0.023). In parenthesis the <sup>4</sup>He concentrations measured by stepped combustion [3] are shown. In most cases the differences between the results obtained by different methods are within reasonable agreements taking into account the associated uncertainties and possible sample heterogeneity. The reason for larger discrepancy for the sample 72501 is not clear. Apart from the sample heterogeneity, formation of dimeric [H<sub>2</sub>]<sub>2</sub><sup>+</sup> ions cannot be ruled out. The H/He ratio for

the samples vary from 7 to 50. It suggests preferential loss of <sup>4</sup>He over H<sub>2</sub> in order to explain the deviations from the solar ratio (17), although a part of the H<sub>2</sub> may have a non-solar origin.

3. Sulphur. The total sulphur concentrations determined using the SO<sub>2</sub> release are (in ppm): 14141 – 970, 15040 – 880, 69921 – 730, and 12070 – 750. These concentrations are well within the range (290 -1400 ppm) determined in lunar soils by other methods [7].

4. Water. The H<sub>2</sub>O concentrations determined in our samples by the described method are (in ppm): 14141 – 120, 15040 – 120, 69921 – 660 and 12070 – 310. These concentrations seem to be higher than actually known for lunar. In our calculations we rely on the assumption that the water transfer from the extraction furnace to the QMS through the metal pipes occurs in a similar way for the soil samples and for the reference material (CaSO<sub>4</sub>\*2H<sub>2</sub>O) even when the pipes are kept at room temperature. This may not be exactly the case.

5. Nitrogen. The nitrogen concentrations in the analysed samples are (in ppm): 14141 – 82 (19), 15040 - 250 (106), 69921 – 220 (108), 12070 - 170 (50-70) and 72501 – 40 (80). In parenthesis the N concentrations determined in the samples by stepped combustion [3] are shown. In most cases the concentrations of nitrogen measured in the present study are higher than expected. There could be multiple reasons for this. Apart from using a poor second order signal at m/z 14 (instead of m/z 28) that increases uncertainty of the calculations, there might also be a contribution from CO at this mass.

6. Carbon. The total carbon concentrations calculated using both CO<sub>2</sub> and CO (as recorded at m/z 12) releases from the lunar soils are (in ppm): 14141 – 290 (210), 15040 – 310 (320), 69921 – 320 (740), 12070 - >70 (250) and 72501 – 160 (400). In parenthesis the C concentrations determined in the samples by stepped combustion [3] are shown. The reasons for the lower calculated than measured by stepped combustion concentrations in few cases are not yet clear and are being currently investigated.

**Conclusions:** The developed QEGA method has been applied successfully for the measurements of Apollo lunar samples. Future applications will likely include measurements of lunar volatiles at the lunar surface through ESA's PROSPECT payload on Luna 27.

**References:** [1] Verchovsky A. B. et al. (2019) *PSS* **181**, 104830. [2] Mortimer J. et al. (2017) *LPSC XCVIII*, abstr. #2113. [3] Mortimer J. et al. (2016) *GCA* **193**, 36-53. [4] Gibson E. K. and Johnson S. M. (1971) *Proc. 2d LSC* **2**, 1351-1366. [5] Assonov S. S. et al. (2002) *MAPS* **37**, 27-48. [6] Bustin R. et al. (1986) *LPSC XVII*, abstract, 95-96. [7] Gibson E. K. (1977) *Phys. Chem. Earth* **X**, 55-62.