CHEMICAL STUDIES OF TWO LUNA-24 REGOLITH SAMPLES

A. V. MURALI, P. B. PAWASKAR *and* G. R. REDDY

Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay–400 085

(*Received 28 March 1979*)

The levels of abundance of twenty major, minor and trace elements have been determined by sequential Instrumental Neutron Activation Analysis (INAA) in two samples (~ 30 mg each) corresponding to 123 cm (123–11) and 190 cm (190–12) depth of the stratified core collected by Luna-24 probe. Both the samples characterized by low TiO (~ 1%) have uniform major element composition and are similar in bulk chemistry to the regolith samples from other layers of Luna-24 core. The two samples are chemically comparable to the local *Mare* basalts except that they contain excess MgO and Cr_2O_3 which could be due to the presence of olivine and/or glass fragments reported from different layers of Luna-24 core samples. The REE and other trace element data of these two samples indicate that (*a*) these samples have very little KREEP component (*b*) sample 190–12 from deepest layer has higher REE content indicating addition (~ 6%) of a third component such as recrystallized breccia to this sample and (*c*) the local fine grained *Mare* basalts form predominant constituents in both the samples.

INTRODUCTION

THE Soviet unmanned Luna–24 probe collected drill core samples from the southeast edge of *Mare Crisium* (north of lunar equator) close to the eastern edge of the visible surface of the Moon. The core tube (8mm diameter) penetrated the regolith to a depth of 225 cm. While the upper 50 cm or so remained empty, the plastic sleeve between 50–220 cm was filled with stratified core sample weighing 170g (Barsukov *et al.*, 1977; Barsukov & Florensky, 1977). Based on the crater density studies three main units of 2.5 b.y., 3.5 b.y. and 3.75 b.y. have been identified (Boyce *et al.*, 1977) in the vicinity of Luna–24 landing site. Spectral reflectance data indicate that the TiO_2 content of Luna–24 landing area is similar to that of *Oceanus procellarum* (Pieters *et al.*, 1976) and the high resolution photographs suggest that the regolith at *Mare Crisium* could contain particles of local mare basalts, the dark mantle material from 20 km east of landing site, highland rock fragments and (probably) the ray material from the Crater Giordano Bruno, 1300 km. away on the lunar farside (Buttler & Morrison, 1977).

Preliminary examination of Luna–24 samples revealed that the Luna–24 soil is relatively immature compared to that of Luna–16 site—the maturity decreasing with depth-and contains high alumina mare basalts with low TiO_2 (~ 1 %) content (Barsukov *et al.*, 1977; Barsukov & Florensky, 1977).

Two ~ 30 mg aliquots of the sample 24123–11 and 24190–12 from Luna–24

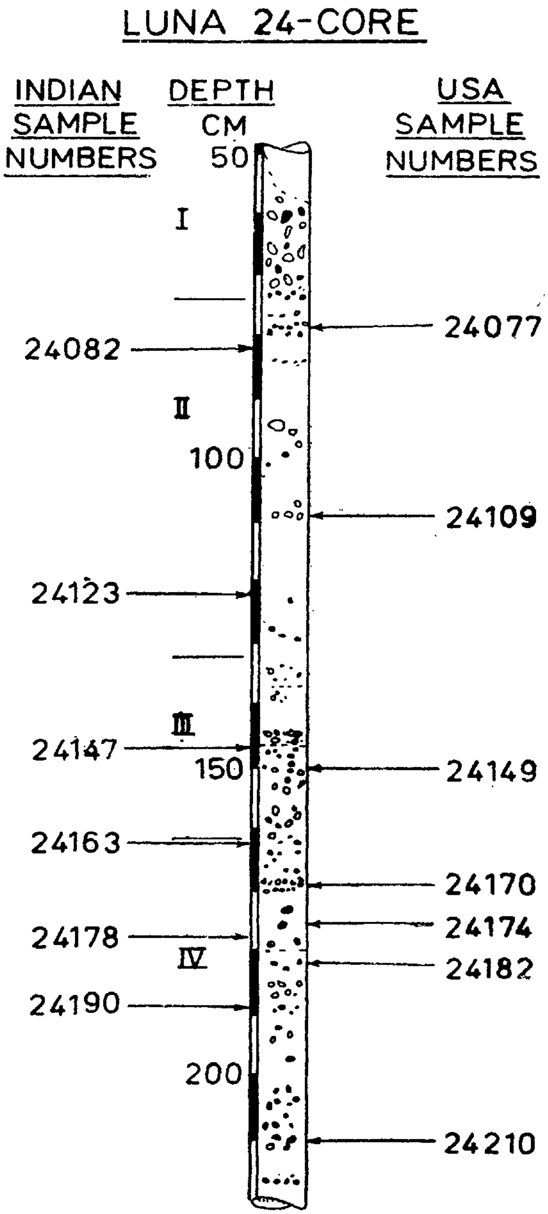

FIG. 1. Sketch (not to scale) of the stratified soils in the Luna-24 Core. I, II, III & IV main units distinguished by USSR scientists. (after Barsukov *et al.*, 1977; Ryder *et al.*, 1977)

core (Fig. 1) have been analysed by us for 20 major, minor and trace elements by sequential Instrumental Neutron Activation Analysis (INAA).

EXPERIMENTAL

The INAA procedure adopted in the present work is identical to the one followed

TABLE I

Sequential INAA procedure adopted for the analysis of Lunar Samples

1. *Short lived nuclides*

Detector : 45 cc Ge (Li)
Analyser : 4K coupled to Pop 8/e computer

Reactor : Cirus; Flux : 10^{13}n cm^{-2} sec^{-1}
Irradiation : Rabbit, 1 min.

Element	Radionuclide	Half-life	Energy (KeV)	Remarks
Ti	^{51}Ti	5.8 min.	320	
Mg	^{27}Mg	9.5 min.	1014	10 minutes cooling 4 minutes counting
V	^{52}V	3.76 min.	1434	
Al	^{28}Al	2.24 min.	1774	
Ca	^{49}Ca	8.7 min.	3084	
Dy	^{165}Dy	2.35h	95	
Mn	^{56}Mn	2.58h	847	Counting after 4 hrs.
Na	^{24}Na	15 h	1369	Counting next day

at Oregon State University, U.S.A. (Wakita *et al.*, 1970; Schmitt *et al.*, 1970). Briefly, the procedure adopted has the following steps.

1. Weighing and sealing of the samples and elemental standards in clean independent double sealed polyethylene bags.
2. Short irradiation and counting for short lived nuclides (Table I.)
3. Longer irradiation followed by sequential counting for long lived nuclides (Table II).

Irradiations have been carried out in the pneumatic and self-serve positions of CIRUS reactor, BARC. The counting assembly consists of a Ge (Li) detector (45 cc) with a resolution (FWHM) of 2.3 KeV at 1332 KeV gamma-ray, coupled to a PDP 8/e based 4096 pulse height analyser system.

RESULTS AND DISCUSSION

Two BCR–1 (Basalt, USGS Standard) and two TKT–1 (Trachyte, Inhouse Standard) control samples of comparable weights have also been sealed identically and irradiated along with the Luna–24 samples each time. It can be seen (Table III) that the values obtained on BCR–1 in the present work are within ± 10 per cent of the reported values (Laul & Schmitt, 1973*b*) while they are within ± 15 per cent (except the value of Co) of the reported values on TKT–1 (Reddy *et al.*, 1976).

Petrographic examination of thin sections of Luna–24 core revealed that the samples from all the layers are made up of ~ 95 per cent of very low Ti (VLT) *Mare* basalt and *Mare* regolith products, the rest being the feldspathic highland rocks, impact melts and homogeneous glasses (Ryder *et al.*, 1977). The VLT Luna–24 basalts have higher Al_2O_3, lower TiO_2 and MgO compared to all other mare basalts and could be further sub-classified into fine grained, coarse grained and meta basalts based on texture and mineralogy (Taylor *et al.*, 1977; Ryder *et al.*, 1977). The difference in major element chemistry between Apollo–17 VLT basalts and Luna–24

TABLE II

Sequential INAA procedure adopted for the analysis of Lunar samples

2. *Long lived nuclides*

Detector : 45 cc Ge (Li)
Analyser : 4K Coupled to PDP 8/e Computer

Reactor : Cirus: Flux : 10^{13} ncm^{-2} sec^{-1}
Irradiation : Self serve posiion, 5h

Element	Radionuclide measured after				Half-life	Energy (KeV)	Interferences
	1 to 2 days	4 days	1 week	1 month			
K	^{42}K	^{42}K			12.4 h	1524	
Na	^{24}Na	^{24}Na			15 h	1369,2754	
La		^{140}La	^{140}La		40.2 h	1596	
Sm		^{153}Sm	^{153}Sm		47 h	103	^{147}Nd(103)
Np		^{239}Np	^{239}Np		2.35 d	228	
Au		^{198}Au	^{198}Au		2.7 d	412	^{152}Eu(411)
Yb		^{176}Yb	^{176}Yb		4.19 d	396	^{147}Nd(396)
Lu		^{177}Lu	^{177}Lu		6.7 d	208	^{176}Yb(209)
Nd		^{147}Nd	^{147}Nd		11.0 d	531	
Ba		^{131}Ba	^{131}Ba		11.7 d	496	
Th				^{233}Pa	27 d	312	^{160}Tb(310)
Cr			^{51}Cr	^{51}Cr	27.7 d	320	^{192}Ir(319)
Ce				^{141}Ce	32.5 d	145	^{152}Eu(146)^{59}Fe(145)
Hf				^{181}Hf	42.4 d	482	^{152}Eu(482)
Fe			^{59}Fe	^{59}Fe	44.6 d	1099	
Ni			^{58}Co	^{58}Cu	71.3 d	811	^{152}Eu(811)
Tb				^{160}Tb	72.3 d	298	^{152}Eu(296) ^{233}Pa(296)
Ir				^{192}Ir	74.2 d	468	
Sc			^{46}Sc	^{46}Sc	83.9 d	1121	
Co			^{60}Co	^{60}Co	5.26 y	1333	
Eu			^{152}Eu	^{152}Eu	12.7 y	122, 1408	^{131}Ba(122)

VLT basalts is that the latter have higher Al_2O_3, CaO, TiO_2 and lower MgO and Cr_2O_3 (Vaniman & Papike, 1977). Taylor *et al.* (1977) explained that Luna–24 basalts could be generated by the fractionation of olivine, low Ca pyroxene and chromite from Apollo–17 VLT basalt magma.

The two Luna–24 samples analysed herein have rather uniform major element composition (Table III) and are identical to the samples from all other layers (Blanchard *et al.*, 1977) indicating that the bulk chemistry is not affected by the presence of different proportions of various constituents viz., basalts, agglutinates, breccias etc. observed (Table I of Ryder *et al.*, 1977). The uniformly higher MgO and Cr_2O_3 in all the layers (our data and that of Blanchard *et al.*, 1977) compared to Luna–24 basalts ($\sim$ 6.5 per cent MgO, 0.2 per cent Cr_2O_3) (Ryder *et al.*, 1977; Taylor *et al.*, 1977) indicates the presence of olivine rich fragments and/or green glass fragments in the samples of predominantly basaltic components.

The trace element content of our two Luna–24 samples indicates that these samples have the lowest rare earth element (REE) content compared to all other lunar soils. This can be seen from Fig. 2, wherein the 190–12 REE values (which has

TABLE III

Elemental abundances in two Luna–24 samples

Element	123–11	190–12	BCR–1		TKT–1	
	29 mg	31 mg	This work	Reported	This work	Reported
			29 mg	Laul & Schmitt (1973*b*)	25 mg	Reddy et al. (1976)
TiO_2%	001.100	001.100	002.400	002.200	000.600	000.560
Al_2O_3%	011.700	012.500	014.100	013.700	014.800	015.280
FeO%	020.100	019.600	012.300	012.300	004.000	003.670
MgO%	011.000	010.000	003.600	003.300	N.d	000.400
CaO%	012.500	011.700	007.100	006.900	001.600	001.620
Na_2O%	000.280	000.330	003.300	003.300	004.000	004.310
K_2O%	000.040	000.030	001.700	001.700	004.100	003.610
MnO%	000.280	000.250	000.170	000.180	000.150	000.180
Cr_2O_3%	000.496	000.503	000.003	000.002	000.002	N.R
Sc ppm	040.000	040.000	030.000	032.000	008.700	009.800
V ppm	150.000	150.000	410.000	410.000	011.000	N.R.
Co ppm	050.000	050.000	033.000	036.000	001.200	001.600
Hf ppm	002.000	003.000	005.200	004.900	019.100	020.000
La ppm	002.800	004.000	026.000	025.000	110.000	120.000
Sm ppm	001.800	002.600	007.000	006.900	013.000	N.R.
Eu ppm	000.610	000.800	001.940	001.950	002.680	003.200
Tb ppm	000.370	000.480	001.010	000.960	001.970	002.300
Dy ppm	003.400	004.200	006.900	006.400	012.000	N.R.
Yb ppm	001.600	002.200	003.200	003.400	009.700	N.R.
Lu ppm	000.270	000.350	000.600	000.520	001.400	N.R.

BCR — 1 — USGS Basalt Standard; N. d : Not detected

TKT — 1 — BARC Trachyte Standard; N.R : Not reported

Estimated errors due to counting statistics are :

Al_2O_3, FeO, Na_2O, MnO, Cr_2O_3, Sc, Co, Sm and Lu ± 1 – 5%; TiO_2, CaO, V, La, E_u and Y_b ± 5 – 10% and MgO, K_2O, Tb and D_y ± 10 – 25%.

higher REE content between the two samples) are plotted against soil values of both *Mare* and highland regions from the eastern half of the moon in the vicinity of *Mare Crisium.* (data from Table I of Laul & Schmitt, 1973*a*). This lower REE content suggests that there is very little KREEP component in Luna–24 samples which has also been pointed out by other workers (Ma & Schmitt, 1977; Papanastassiou *et al.*, 1977).

Between the two Luna–24 samples analysed by the present authors, the sample from the top layer, i.e., 123–11 has lower REE content (~8X) compared to the 190–12 (~ 12X) sample from the bottom. This is consistent with the petrographic observation that the deepest layer of Luna–24 core has the highest percentage of regolith products (Ryder *et al.*, 1977). Identical REE trends and the same degree of negative E_u anomaly ($S_m/E_u \sim 3$) in both the samples, suggests that this could be due to different amounts of olivine present in the two samples (olivine has low REE distribution

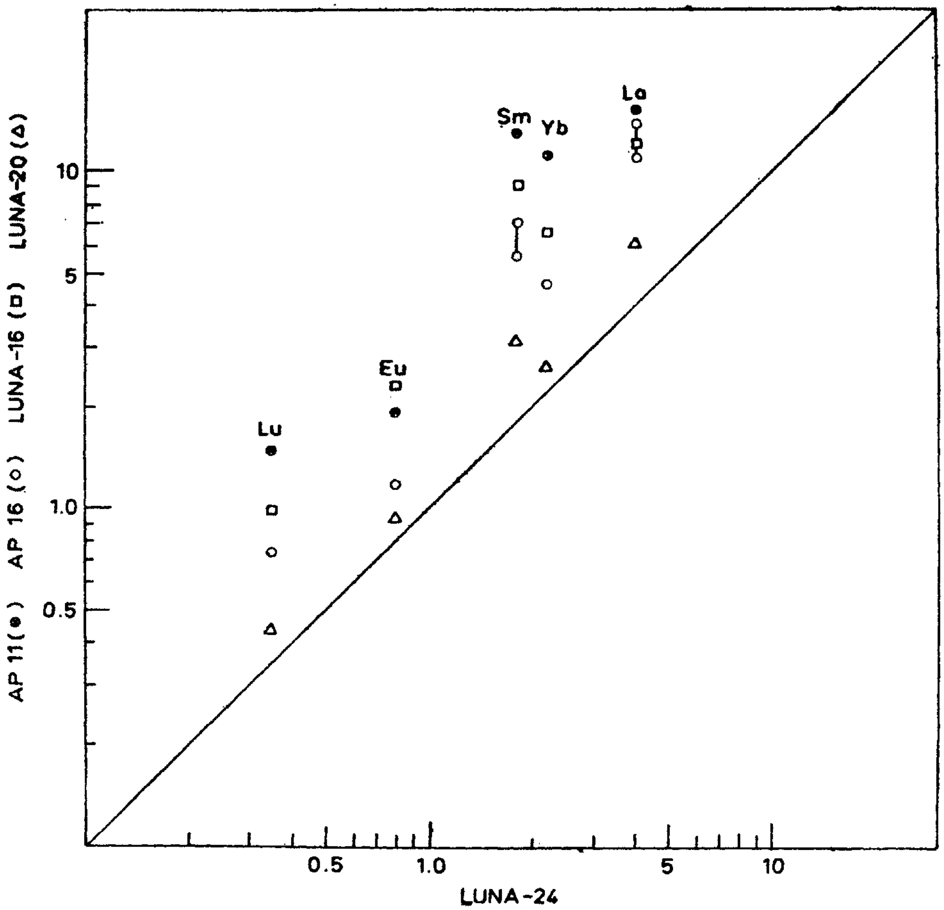

FIG. 2. Abundances of REE of Luna-24 soil (190–12) *vs.* soil data from other Missions. (Data from Laul and Schmitt, 1973*a*; $\overset{o}{\underset{o}{|}}$ -Ranges.)

coefficients and hence if present, does not alter the REE trends and S_m/E_u ratios but dilutes the overall abundance of REE). However, similar Cr_2O_3, Sc, Co and V contents (i.e., the elements with higher distribution coefficients for olivine) in both the samples rules out this differences as due to 'olivine dilution' alone. Blanchard *et al.* (1977) observed a bimodal distribution in the Luna-24 soils i.e., < 20 μm more mature fraction with 16X REE and a coarser 90–150 μm fraction with 7X REE contents. The higher REE trend is attributed to the presence of small amount of recrystallized breccia component (24077, 17). While our 123–11 is very much comparable to their average bulk soil values, the sample 190–12 needs addition of $\sim$ 6 per cent recrystallized breccia component (Fig. 3) to account for the excess REE. This mixing model is consistent with the lack of any significant variation in Cr_2O_3, Sc, Co and V because the recrystillised breccia is depleted in these elements.

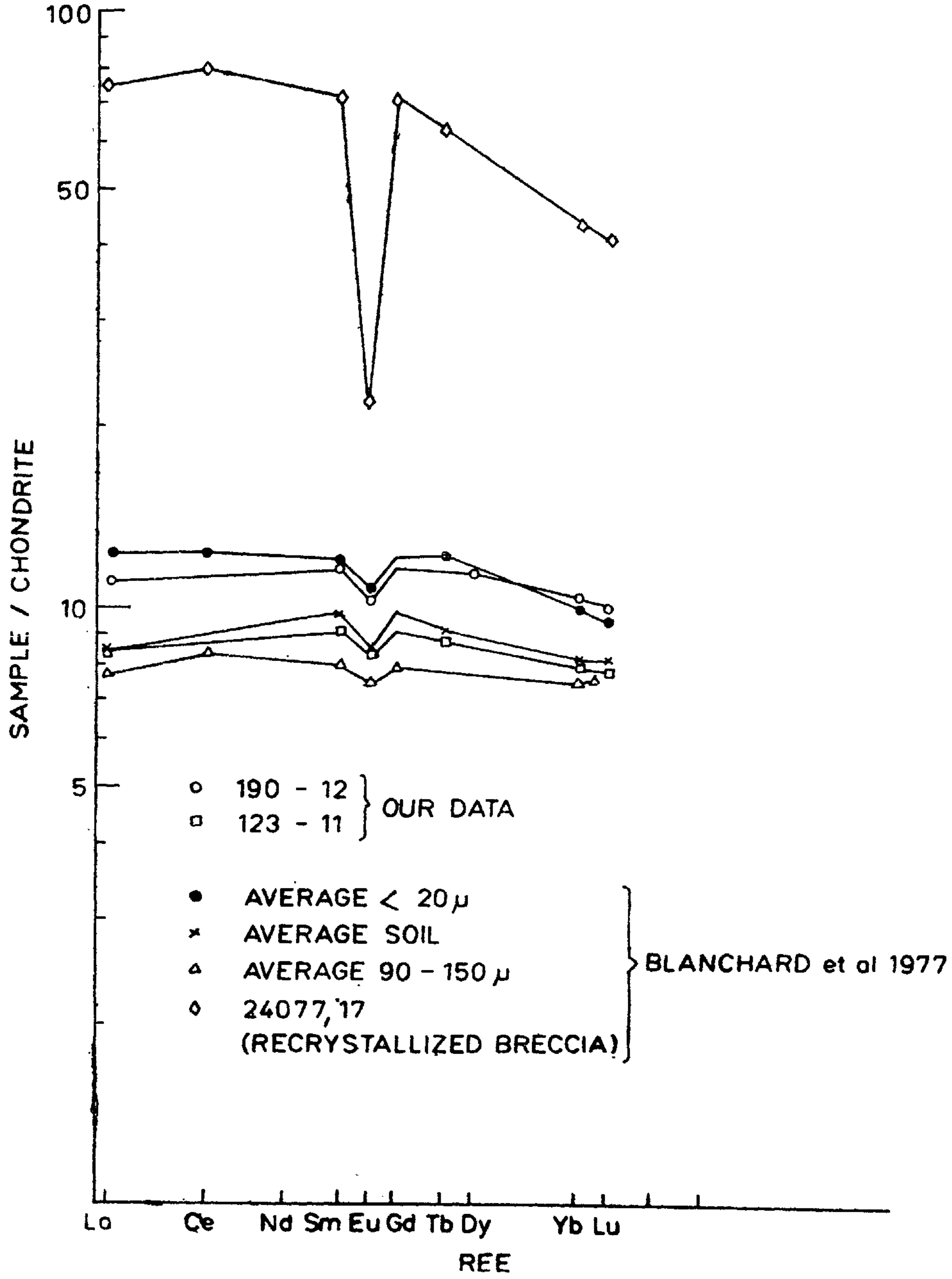

FIG. 3. Luna-24 REE data compared to the data of two main size fractions (< 20µ and 90–150µ) observed in Luna-24 soils.

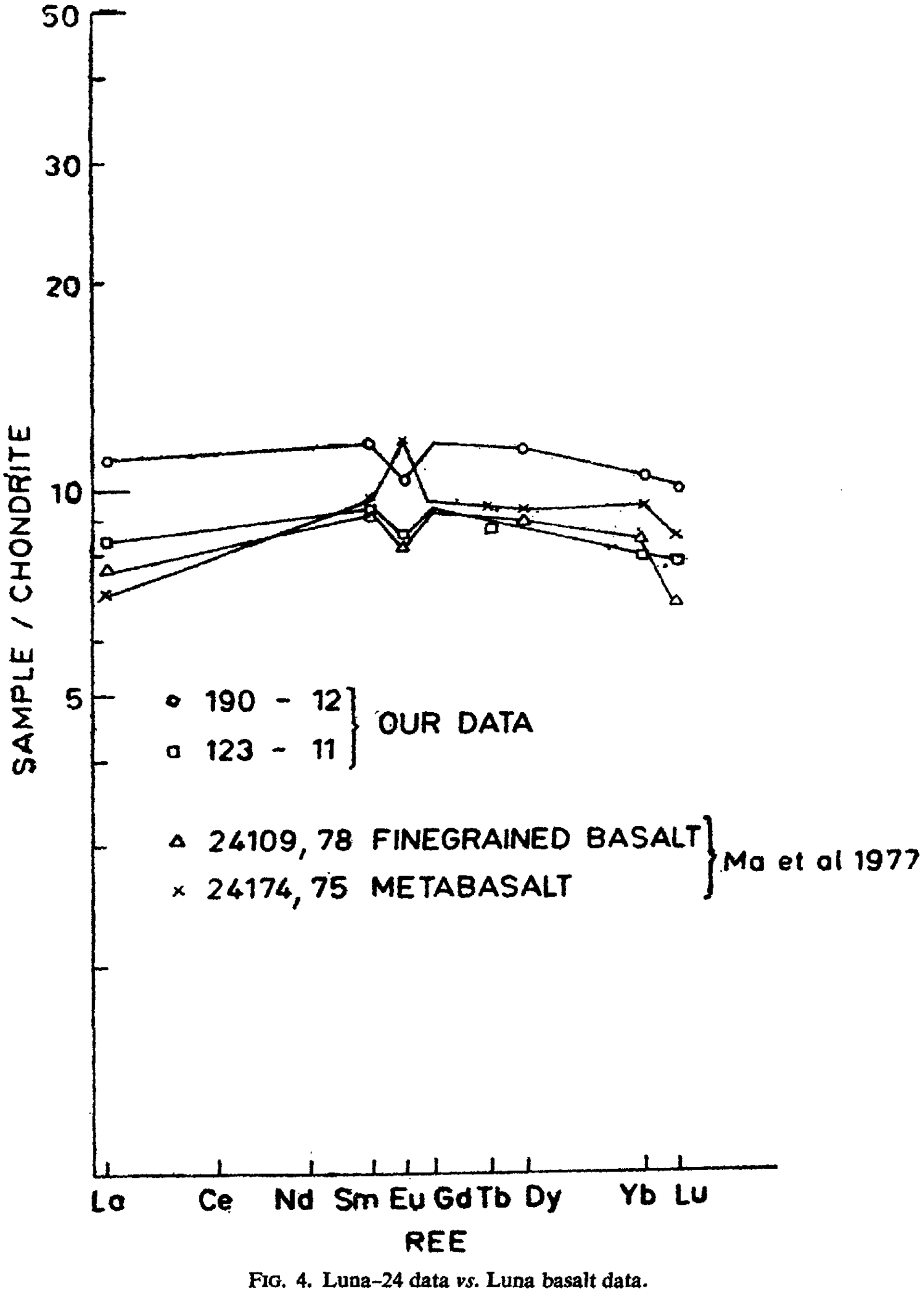

FIG. 4. Luna-24 data *vs.* Luna basalt data.

Ma *et al.* (1977) have analysed different types of Luna-24 mare basalts and found that all of them have very low TiO_2 (except 24149 with 2.3 per cent TiO_2 which they attribute to heterogeneous ilmenite content) and have comparable major element content. However, their trace element data indicate that while the fine grained basalts have negative europium anomaly, the meta-basalts and few coarse grained basalts have different REE patterns and positive E_u anomalies. Both 123-11 and 190-12 have REE patterns identical to the fine grained basalts (Fig. 4) indicating the predominance of fine grained basaltic component in these samples.

ACKNOWLEDGEMENTS

The authors are thankful to Dr. M. Sankar Das, Head, Analytical Chemistry Division for valuable suggestions and encouragement. Thanks are also due to the U.S.S.R. Academy of Sciences for providing Luna-24 samples and theIndian National Science Academy for coordinating these studies and Professors D. Lal, F.N.A. and N. Bhandari for helpful discussion and their interest in the work.

One of the authors (AVM) is very much indebted to Professor R. A. Schmitt (Oregon State University, USA) and Dr. J. C. Laul, (formally of OSU presently at pacific Northwest Laboratories Richland, Washington) for the training in INAA and introducing him to Lunar work during his tenure as a post-doctoral fellow at OSU.

REFERENCES

Barsukov, V. L., and Florensky, C. P. (1977). The lunar soil from *Mare Crisium* preliminary data. *Lunar Sci.*, VIII, 61-63.

Barsukov, V. L., Ivanov, A. V., Nazarov, M. A., Rode, O. D., Stakeev, Yu. I., Tarasov, L. S., Tobelko, K. I., and Florenski, C. P. (1977). Preliminary description of the regolith core from *Mare Crisium*. *Lunar Sci.*, **VIII**, 67-69.

Blanchard, D. P., Haskin, L. A., Brannon, J. C., and Aaboe, E. (1977). Chemistry of soils and particles from Luna-24. *Conf. Luna*-24, 37-40.

Boyce, J. M., Schaber, G. G., and Dial, A. L. (1977). Age of Luna-24 *Mare* basalts based on crater studies. *Nature*, **265**, 38-39.

Butler, P (Jr)., and Morrison, D. A. (1977). Geology of the Luna-24 landing site. *Lunar Sci.*, **VIII**, 151-153.

Laul, J. C., and Schmitt, R. A. (1973*a*). Chemical composition of Luna-20 rocks and soil and Apollo-16 soils. *Geochim. Cosmochim. Acta*, **37**, 927-942.

———(1973*b*). Chemical composition of Apollo-15, 16 and 17 samples. *Proc. 4th Lunar Sci. Conf. Geochim. Cosmochim. Acta*, **2**, 1349-1367.

Ma, M. S., and Schmitt, R. A. (1977). Luna-24 soils: a chemical study. *Conf. Luna*-24, 98-101.

Ma, M. S., Schmitt, R. A., Taylor, G. J., Warner, R. D., Lange, D. E., and Keil, K. (1977). Chemical and petrographic studies of 18 Luna-24 lithic fragments. *Conf. Luna*-24, 102-105.

De Paolo, D. J., McCulloch, M. T., Papanastassiou, D. A. Huneke, J. C., and Wasserburg, G. J. (1978). Ages and evolution of Luna-24 samples. *Lunar planet. Sci.*, **IX**, 244-246.

Pieters, C., Mc Cord, T. B., and Adams, J. M. (1976). Regional basalt types in the Luna-24 landing area as derived by remote observations. *Geophys. Res. Lett.*, **3**, 697-700.

Reddy, G. R., Pant, D. R., Rao, B. L., and Sankar Das, M. (1976). Neutron activation analysis of 13 minor and trace elements in geological samples. *J. radioanal. Chem.*, **33**, 39-51.

Ryder, G., McSween, H. Y. (Jr)., and Marwin, U. B. (1977). Basalts from *Mare Crisium. The Moon*, **17**, 263–288.

Schmitt, R. A., Linn, T. A. (Jr)., and Wakita, H. (1970). The determination of fourteen common elements in rocks *via* sequential instrumental activation analysis. *Radiochim. Acta*, ,**13**, 200–212.

Taylor, G. J., Warner, R., Wentworth, S., Keil, K., and Sayeed, U. (1977). Petrology and chemistry of Luna–24 mare basalts and basaltic glasses. *Conf. Luna*–24, 189–192.

Vaniman, D. T., and Papike, J. J. (1977). Ferrobasalts from *Mare Crisium* : Luna–24. *Geophys. Res. Lett.*, **4**, 497–500.

Wakita, H., Schmitt, R. A., and Rey, P. (1970). Elemental abundance of major, minor and trace elements in Apollo–11 lunar rocks, soil and core samples. *Proc. Apollo*–11 *Lunar Sci. Conf.*, I, 1685–1717.