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"New" lunar meteorites: Implications for composition of the global lunar surface, lunar crust, and the bulk Moon

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Abstract-New data for lunar meteorites and a synthesis of literature data have significant implications for the interpretation of global Th data and for the Moon's bulk composition. As presently calibrated (Prettyman et al. 2002), the Lunar Prospector gamma-ray data imply that the average global surface Th = $1.58 \mu g/g$. However, that calibration yields implausibly high concentrations for the three most Th-poor documented sampling sites, it extrapolates to a nonzero Lunar Prospector Th, $\sim 0.7 \,\mu g/g$, at zero sample Th, and it results in a misfit toward too-high Th when compared with the global regolith Th spectrum as constrained using mainly lunaite regolith breccias. Another problem is manifested by Th versus K systematics. Ground truth data plot consistently to the high-Th/K side of the Prospector data trend, offset by a factor of 1.2. A new calibration is proposed that represents a compromise between the Th levels indicated by ground truth constraints and the Prettyman et al. (2002) calibration. Conservatively assuming that the Th versus K issue is mostly a K problem, the average global surface Th is estimated to be $\sim 1.35 \,\mu$ g/g. The Moon's remarkable global asymmetry in KREEP abundance is even more pronounced than previously supposed. The surface Th concentration ratio between the hemisphere antipodal to the Procellarum basin and the hemisphere centered on Procellarum is reduced to 0.24 in the new calibration. This extreme disparity is most simply interpreted as a consequence of Procellarum's origin at a time when the Moon still contained at least a thin residual layer of a global magma ocean. Allowing for diminution of Th with depth, the extrapolated bulk crustal Th is ~0.73 μ g/g. Further extrapolation to bulk Moon Th yields ~0.07 μ g/g, which is nearly identical to the consensus estimate for Earth's primitive mantle. Assuming chondritic proportionality among refractory lithophile elements implies Al₂O₃ of approximately 3.8 wt%. The Moon's bulk mantle mg ratio is only weakly constrained by seismic and mare-basaltic data. KREEPand mare-free lunaite regolith samples, other thoroughly polymict lunar meteorites, and a few KREEP-free Apollo highland samples manifest a remarkable anticorrelation on a plot of Al₂O₃ versus mg. This trend implies that an important component of the Moon is highly magnesian. The bulk Moon is inferred to have an Earth-like oxide mg ratio of \sim 87–88 mol%. The close resemblance between the bulk Moon and Earth's primitive mantle extends to moderately volatile elements, most clearly Mn. Unless major proportions of Cr and V are sequestered into deep mantle spinel, remarkably Earth-like depletions (versus chondrites) are also inferred for bulk Moon Cr and V.

INTRODUCTION

The 25–30 lunar meteorites (lunaites) represent a valuable adjunct to the rocks acquired by the Apollo missions from a limited region of the Moon's central near side (a polygon can be drawn around the six Apollo sites to encompass a mere 2.7% of the Moon's surface). Lunaite source craters are probably distributed almost randomly across the Moon's surface (Gladman 1996). In contrast, the clustering of the Apollo sites in the central near side

notwithstanding, site-to-site variation among Apollo rocks is generally much greater between missions (the average separation from the nearest-neighbor site is 420 km) than between two ends of a single mission's traverse range (separations \leq 11 km, half <2 km).

Besides lunaites, the limitations of the Apollo sampling of the Moon are mitigated by very limited ("fines" only) sampling from three Luna sites, but these are tightly clustered (the maximum separation is 444 km) in an east-central nearside area not far from the Apollo sampling region

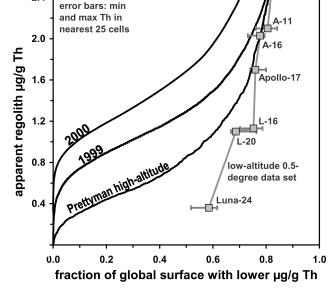


Fig. 1. Low end of the global spectrum of regolith Th concentrations, plotted as a function of fractional abundance relative to the total lunar surface, as calibrated by Lawrence et al. (1999, 2000) and Prettyman et al. (2002). Shown for comparison is the global spectrum as constrained by the Th rankings of Apollo/Luna regolith sampling sites according to low-altitude, 0.5 degree per pixel, LP-GRS data (Lawrence et al. 2000). For simplicity, "error bars" are shown only for the Apollo/Luna x-axis data; y-axis uncertainties may be gleaned from Table 1.

(entirely within the 0.09 lunar circumferences of Apollo 17). Orbital spectrometry has also furnished data for surface (regolith) composition (e.g., Metzger et al. 1977; Lawrence et al. 2000, 2003) that is global in coverage, but only for a few elements and with limited sensitivity and precision. These orbital data indicate a remarkable degree of 1000 km scale heterogeneity, especially in terms of abundance of thorium and other incompatible elements (Lawrence et al. 2003; Elphic et al. 2000b). The main focus of this paper is to employ old data and new data (Warren et al. Forthcoming) for lunaites, along with Apollo and Luna samples, as ground truth with which to test and, if necessary, improve the current calibration (Prettyman et al. 2002; Lawrence et al. 2003) of the Lunar Prospector gamma-ray spectrometry (LP-GRS) data for thorium. The ultimate goal is to estimate the bulk composition of the whole Moon and its crust as constraints on the Moon's evolution and especially of its origin.

Thorium is a key element for several reasons. Thorium is a natural source for several large γ -ray peaks and thus is exceptionally well suited to the LP-GRS technique. Geochemically, Th is the exemplar of a large suite of refractory-incompatible elements, including all of the rareearth elements except Eu. On the Moon, these elements, along with a few volatile-incompatible elements (K, Rb, and Cs), are strongly correlated and are concentrated in the distinctive crustal component KREEP (Warren and Wasson 1979a). It is widely assumed that all the refractory-lithophile elements, including the major elements aluminum and calcium, are in chondritic or near-chondritic proportions with one another in bulk planets (e.g., Taylor 1982; Hart and Zindler 1986; Sanloup et al. 1999). Thus, by constraining the bulk Moon content of Th, we establish a foundation for constraining the overall composition of the Moon. The distribution of Th is also important because the KREEP-linked radioactive elements Th, U, and K generate internal heat and because Th is a tracer for petrologically "evolved" crust. Apart from Th, the lunaites also help to constrain the key parameter of the overall mg (=Mg/(Mg + Fe)) ratio of the lunar mantle.

ORBITAL Th RESULTS VERSUS GROUND TRUTH: APOLLO/LUNA SAMPLES

Problems with Past LP-GRS Th Calibrations

The original LP-GRS calibration (Lawrence et al. 1999) implied an average global regolith Th of 1.82 μ g/g. Lawrence et al. (2000) revised this by applying simple factor of 4/3 correction to the total data set, which yielded average global regolith Th of 2.40 μ g/g. Prettyman et al. (2002) used a fundamentally different approach to derive a calibration for a low spatial-resolution (5 degree) data set with average global regolith Th of 1.58 μ g/g; this calibration was adapted to high spatial resolution (0.5 degree) by Lawrence et al. (2003).

Orbital GRS Th calibrations can be tested by comparison both with the Apollo/Luna type samples of documented site origin and with the populational traits (ignoring location constraints) of the Apollo/Luna samples plus lunaites. Both techniques will be employed in this paper. The Lawrence et al. (2000) upward revision was based in part on a discrepancy at the high end of the Th range, i.e., versus the Apollo 14 samples. However, Gillis et al. (2000; cf. Haskin et al. 2000) and Warren (2000) noted that the early LP-GRS calibrations (Lawrence et al. 1999, 2000) also appeared faulty at the low end, as they led to intercepts far from zero when the LP-GRS results for documented sampling sites were plotted against ground truth data. Warren (2000) found further indications of the same problem based on comparison between the global spectrum of LP-GRS Th data and the global spectrum implied by samples.

Independent of sample data, just the shape of the global LP-GRS Th spectrum (Fig. 1) is a further indication of the same zero-offset problem. In Fig. 1, the three sigmoidal curves show the low-Th end of the global spectrum of regolith Th concentrations in the orbital LP-GRS data sets of Lawrence et al. (1999, 2000) and Prettyman et al. (2002). If the low end of the calibration were accurate, the spectrum would be unlikely to show such a sharp downturn in Th concentration at the low-Th end of the spectrum, ranging, in the worst case (Th₂₀₀₀), all the way from zero to 0.6 μ g/g in the first 1.5% of the pixels. From 0 to ~1 μ g/g Th, the older

2.4

calibrations, and to a lesser degree even the Prettyman et al. (2002) calibration (Th₂₀₀₂), yield curves with shapes resembling one half of the familiar bell curve of the probability density function of the normal distribution. This is a remarkable coincidence. A more plausible natural distribution would have Th concentration leveling off at some low value in the most KREEP-poor highland areas of the Moon, and thus the curves on Fig. 1 would remain concave-up (as at higher Th) throughout the distribution, instead of turning concave-down at ~0.5–1.2 µg/g.

Warren (2000 and the preliminary version of this paper; cf. Lawrence et al. 2003) showed that at least for the Lawrence et al. (1999, 2000) calibrations, the resemblance of the LP-GRS data spectrum to the bell curve is an artifact of the zero-offset problem. Warren (2000) traced the zero-offset problem to an explicitly stated assumption of Lawrence et al. (1999, 2000): that the pixel with the minimum counting rate (latitude 36°N, longitude 117°E) was defined to have Th = 0 μ g/g. At first glance, this assumed Th concentration seems conservatively low; surely, nowhere on the Moon is the regolith Th content absolutely zero. The assumption did indeed lead to a calibration error, but only because 0 µg/g is actually too high for this purpose. The data set consisted of over 11,000 cells, a large fraction of which potentially have (and which, as will be shown below, in fact do have) regolith That very low levels, comparable to the 1 σ uncertainty in the final data. In such a circumstance, many cells will scatter below their true concentration levels along a bell-curve-like statistical trend and a few will inevitably yield apparent Th concentrations 3–4 σ below the real values. In consequence, anchoring the lowest apparent concentration to 0 instead of some (preliminarily) negative value will lead to an offset of nearly all data by $3-4\sigma$, which in practice translated into well over 1 μ g/g (Warren 2000). Even though this 0 Th anchor assumption has been explicitly (Lawrence et al. 2003) dropped from the most recent LP-GRS calibration (Prettyman et al. 2002), optimizing the calibration near the low end of the compositional range remains a daunting challenge.

Documented-Location Samples and the Latest Calibration

For making comparisons with documented Apollo/Luna samples, regolith samples (soils and regolith breccias) are more useful than other sample types (fragmental and impact melt breccias). The orbital GRS measurements pertain to regolith. Moreover, regolith samples tend to show limited compositional diversity within any small region of the Moon much more than other lunar materials (Warren 1994; Korotev et al. 2003). Their compositions tend to closely follow the average composition of the underlying crust (albeit always dampened, in a statistical way, by contributions from more distant sources), which makes them good indicators of regional variations in crustal composition. The variability at any given site is greater for regolith breccias than for evolving soils (lunaite regolith breccias attest to the occasional displacement of regolith breccias over great distances), but the vast majority of regolith breccias at a given locale are similar in bulk composition to local soils (McKay et al. 1986, 1989).

The typical surface resolution of a low-altitude LP-GRS measurement, 40-50 km (Lawrence et al. 2000), is far broader than the longest traverse on any Apollo mission. Thus, for ground truth purposes, the best approach is to average all regolith sample compositions from each Apollo/ Luna site. Such averages are available from numerous sources (e.g., Haskin and Warren 1991; Korotev 1998), and Table 1 gives a slightly revised compilation. The corresponding LP-GRS data are not necessarily individual pixels, because in some cases the sampling site is near (or even straddles) a side or corner of its LP-GRS pixel. Also, some of the sites are uncommonly heterogeneous on the relevant 10-100 km scales because they are on maria close to mare/highland boundaries: Apollo 15, Apollo 17, and the especially difficult Apollo 12. The Apollo 12 landing site was on a mare lava terrain, but one of limited extent with highland terrains in close proximity in several directions.

Table 1 also includes a set of LP-GRS results derived by interpolation from the most recent published calibration: Prettyman et al. (2002), hereafter Th_{2002} . The Th_{2002} calibration is for a map with 5 degree spatial resolution, much lower than a previous (Lawrence et al. 2000) 0.5 degree map. Lawrence et al. (2003) have published a high-resolution (0.5 degree) map, but not yet a full pixel-by-pixel data set, based on adapting the Th₂₀₀₂ calibration to the same raw data as for the Lawrence et al. (2000) data set. For this work, I have also derived a 0.5 degree data set based on the Th_{2002} calibration. For applying the 5 degree Th_{2002} calibration to a 0.5 degree spatial resolution data set, all pixels in the Th_{2002} data set were first sorted in order of increasing Th. The resultant sorted version of the Th₂₀₀₂ data set was utilized to develop a precise polynomial equation for the cumulative proportion of the global surface at and below a given Th concentration level. This polynomial equation was converted into a polynomial expression for Th concentration level at any given cumulative proportion of the global surface. In practice, I used a set of several equations, optimized for different portions of the Th range; back-conversion calculations, as checks, showed negligible errors. Combination of this polynomial expression with a Th-sorted variant of the 0.5 degree (Planetary Data System 2001) version of the Lawrence et al. (2000) data set resulted in a precisely scaled translation of Th_{2002} into a 0.5-degree data set ($Th_{2002.5}$).

As a check on the accuracy of this translation method, the average global surface Th implied by the $Th_{2002.5}$ data set is 1.57 µg/g, precisely the same as implied by the original Th_{2002} data set. There presumably is a problem with the translation, however, at the extreme high end of the Th range. Improving the high end of the calibration is not a goal of this work, but it

	-		Ground truth from sample	Grour	Ground truth from samples	amnles					
			Local mare basalt	Haskin	Korotev	This work			Comments regarding the representativeness	ing the represer	itativeness
Site	Latitude	Longitude	Th, μg/g	Th, μg/g	Th, μg/g	Th, μg/g	LP-GRS Th, µg/g	h, μg/g	of GRS pixel versus the sampled regolith	sus the sample	d regolith
Apollo 11	0.67	23.49	~2	2.3 ± 0.7	1.94 ± 0.11	2.1 ± 0.2	3.21	[2.36]	Relatively simple mare terrain	mare terrain	
Apollo 12	-3.20	-23.38	0.78	5.2 ± 1.2	3.6–9.7	6.0 ± 2.0	7.1	[6.3]	Samples are highly diverse	ly diverse	
Apollo 14	-3.67	-17.47	2.3	~15	12.7 ± 0.2	13.3 ± 0.5	11.6 ^a	$[9.8^{b}]$	See text		
Apollo 15	26.43	3.65	0.57	~4	1.5–3.5	3.7 ± 1.3	5.3 ^a	$[4.5^{a}]$	Samples are highly diverse	ly diverse	
Apollo 16	-9.00	15.52	I	~2	1.0 - 2.22	2.0 ± 0.3	2.9ª	$[2.0^{a}]$	Relatively simple highland terrain	highland terrai	n
Apollo 17	20.17	30.77	0.3	2.4 ± 0.6	0.7 - 3.0	1.7 ± 0.8	2.75	[1.84]	Samples are highly diverse	ly diverse	
Luna 16	-0.68	56.30	1.9	Ι	1.17 ± 0.13	1.13 ± 0.17	2.69	[1.78]	Single sample of mare terrain	mare terrain	
Luna 20	3.53	56.55	I	~0.98	1.2 ± 0.3	1.10 ± 0.14	2.32	[1.37]	Single sample of highland terrain	highland terrair	
Luna 24	12.75	62.20	0.19	0.40 ± 0.09	0.36 ± 0.05	0.36 ± 0.06	1.89	[1.04]	Single sample of mare terrain	mare terrain	
^a Weighted aver ^b For Apollo 14,	age of multiple, the Th-freque	e pixels (e.g., lan arcy based extrap	^a Weighted average of multiple pixels (e.g., landing site is near a pixel side or corner; see text). ^b For Apollo 14, the Th-frequency based extrapolation is probably invalid (spuriously low) because the 0.5 degree data set resolves small regions of extreme Th enrichment far better than does the Prettyman	side or corner; see did (spuriously low	text).) because the 0.5	degree data set res	olves small regi	ons of extrer	ne Th enrichment far	better than does	the Prettyman
et al. 5 degree	et al. 5 degree data set (see text).	ext).	•	•		1	•				
LP-GRS data a	re from the Pla	metary Data Syst	LP-GRS data are from the Planetary Data System's (July 2001 release) 0.5 degree version of the Lawrence et al. (2000) calibration; shown in [brackets] is an extrapolation from that data set) 0.5 degree version	n of the Lawrence	et al. (2000) calibi	ation; shown in	[brackets] i	s an extrapolation fro	om that data set	:
matching the but include Ha	I h-frequency s askin and Warr	pectrum of the P en (1991), Korot	matching the 1h-frequency spectrum of the Prettyman et al. (2002) calibration (see text). Data source for ground truth (averages of soil at but include Haskin and Warren (1991), Korotev (1998), and the many individual references cited on p. 464 of Haskin and Warren (1991).	alıbratıon (see text) y individual referen	. Data source for ces cited on p. 46	ground truth (aver 4 of Haskin and W	iges of soil and arren (1991).	regolith bree	calibration (see text). Data source for ground truth (averages of soil and regolith breccia analyses) are too numerous to list in full, ny individual references cited on p. 464 of Haskin and Warren (1991).	numerous to list	ın tull,
Table 2. Su	mmary of l	iterature data	Summary of literature data for K, Th, and U in three east-central nearside (Luna) regolith samples.	in three east-o	entral nearsid	e (Luna) regol	ith samples.				
	•			Luna 16, 0.68°S, 56.3°E	8°S, 56.3°E	Luna 2	Luna 20, 3.53°N, 56.55°E	5.55°E	Luna 24,	Luna 24, 12.75°N, 62.2°E	°E
				K	Th U	K	Th	N	К	Th	N
Reference		Tech	Technique	mg/g	н <u>в</u> /вн	µg/g mg/g	pg/g	µg/g	mg/g	g/gn	µg/g
Maria and Di	Maria and Dhilnotte (1073)		Atomic absorption			0 56					
Barsukov et al. (1977)	eren) suuquu al (1977)		NAA Kolesov lah			00.0				[1 04]	[0 26]
Kolesov and	Kolesov and Surkov (1980)		INAA. Kolesov lab						[0.33]	[0.53]	[0.21]
Surkov et al. (1975)	. (1975)		INAA, Kolesov lab	1.0	0.9	[0.70]	[0.84]				
Blanchard et al. (1978)	t al. (1978)	INAA	A			1	1		0.25	0.31	
Bobrov et al. (1980)	. (1980)	INAA	Α							0.46	[0.95]
Cimbalniko	Cimbalnikova et al. (1977)	7) INAA	Α	1.2	1.1 [0	[0.7] 0.50	0.9	[0.75]			
Gangadhara	Gangadharan et al. (1974)		A	1.29							
Gillum et al. (1972)	. (1972)	INAA	A	1.0							
Helmke and	Helmke and Haskin (1972)	2) INAA	Α	0.91							
Jerome et al. (1972) ^a	. (1972) ^a	INAA	Α	0.865	1.13		0.95				
Korotev et al. (1990a)	d. (1990a)	INAA	A		1.14 [0	[0.19]					
Korotev et al. (1990b)	.l. (1990b)	INA	INAA, 88 cm level							0.29	0.15
Korotev et al. (1990b)	.d. (1990b)	INA	INAA, 105 cm level							0.33	<0.3
Kuznetsov a	Kuznetsov and Styf (1989)		Α		0.89						
Laul and Schmitt (1973)	hmitt (1973)	INAA	Α				1.0	<0.5			
Laul et al. (1981)	(1861)	INA	INAA, bulk soil	0.91	1.39 [0	[0.4] 0.56	1.32		0.22	0.40	
Laul et al. (1981)	(1861)	INA	INAA, sieving	0.91		.4] 0.56	1.22		0.29	0.30	
Ma et al. (1978))78)	INAA	Α						0.23	0.42	

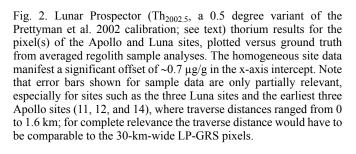
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Table 1. A comparison of LP-GRS thorium results versus ground truth (samples) data.

K mg/g 0.98 0.97 0.85	Th μg/g	U Ug/g	К	Th	11	Л	Ē	11
mg/g 0.98 0.97 0.85	H8/8	ភ/ភព			0	4	Πh	
0.84 0.98 0.97 0.85		ra ra	mg/g	µg/g	μg/g	mg/g	µg/g	µg/g
0.84 0.98 0.97 0.85						0.29		
0.98 0.97 0.85		$[0.3]^{b}$						
0.97 0.97 0.85			0.58		0.37			
0.97 0.97 0.85			0.55					
0.97		0.34						
0.85		0.39						
0.85			0.55					
0.85						0.23		
0.85						0.26		0.113
				1.21	0.33			
	1.17	0.32						
				1.13	0.30			
				1.04	0.30			
			[0.75]	[0.73]	[0.22]			
						[0.3 - 0.4]	[1.3 - 1.4]	[0.4]
	[1.6]			[1.4]			[0.83]	
					0.31			
		[0.38]			[0.44]			
								[0.0]
[2.08]						[0.73]		
						[0.50]		
0.87	[0.47]	[0.10]						
0.83	[0.8]	[0.25]	[0.8]	[0.2 - 1.5]	[0.07 - 0.5]			
[0.91]	[1.1]	[0.3]	[0.64]	[1.0]	[0.29]			
0.96	1.13	0.35	0.56	1.10	0.32	0.24	0.36	0.13
0.13	0.17		0.03	0.14	0.03	0.03	0.06	
	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		1.17 [1.6] [1.6] [0.8] [1.1] [1.1] 0.17	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{bmatrix} 1.17 & 0.32 & & 1.21 & 0.33 \\ 1.17 & 0.32 & & 1.13 & 0.30 \\ & 1.04 & 0.30 & & 0.30 \\ & 1.04 & 0.30 & & 0.31 \\ & & & & 0.31 & & 0.31 \\ & & & & & & 0.31 & & 0.31 \\ & & & & & & 0.31 & & 0.31 \\ & & & & & & & 0.31 & & 0.31 \\ & & & & & & & 0.31 & & 0.31 \\ & & & & & & & 0.31 & & 0.31 & & 0.31 \\ & & & & & & & & 0.31 & & 0.31 & & 0.31 \\ & & & & & & & & & 0.31 & & 0.31 & & 0.31 \\ & & & & & & & & & 0.31 & & 0.31 & & 0.31 & & 0.31 \\ & & & & & & & & & & 0.31 & & 0.32 & & 0.30 & & 0.14 & & 0.03 & & 0.0$

"New" lunar meteorites

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6

Th (µg/g) from GRS (Prettyman-interpolated calibration)

8

10

12

14

should be noted that near the high-Th end of the calibration the true Th diversity is probably artificially dampened into a clustering of relatively moderate results. This dampening is expected because, as Lawrence et al. (2003) have very effectively shown, there are major variations in Th at scales smaller than the 5 degree (152 km) scale of the Th_{2002} data set. There is no analogous problem at the low end of the Th range. The lowest Th levels are found in giant, 1000-km-scale regions of uniformly Th-poor farside and limb highlands; the LP-GRS technique was not sensitive or precise enough to accurately measure whatever limited diversity may exist within these extremely Th-poor regions. For present purposes, the only significant aspect of this shortcoming of the high-end portion of the Th_{2002 5} data set is that the Th_{2002 5} result for Apollo 14 (Table 1, Fig. 2) is untrustworthy (apart from Table 1 and Fig. 2, the Th_{2002.5} data set is not used in this paper).

When ground truth data for the other eight Apollo/Luna sites are compared with the Th_{2002.5} LP-GRS results, an excellent correlation is found (Fig. 2). However, the fit is poor, inasmuch as the trend's intercept with the LP-GRS axis comes at Th $\approx 0.7 \ \mu g/g$, or slightly lower (0.4 $\mu g/g$) if the heterogeneous sites Apollo 12, 15, and 17 are given full weight in the fit. This intercept result represents a vast improvement over earlier LP-GRS calibrations, which, as noted by Warren (2000) and Haskin et al. (2000), intercepted

the LP-GRS axis at ~1.6 μ g/g. But the intercept remains significantly greater than zero.

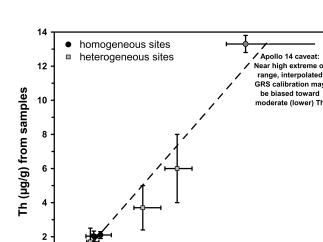
An even clearer manifestation of a lingering problem at the low end of the LP-GRS Th calibration can be found by examining the relative Th-concentration rankings of the documented Apollo/Luna regoliths within the global spectrum of regolith concentrations in a 0.5 degree LP-GRS data set (Th₂₀₀₀, the Planetary Data System version of Lawrence et al. 2000) based on the same raw data as the most recent (Lawrence et al. 2003) LP-GRS data set. The first step in this procedure is again to sort and plot all of the LP-GRS results in order of increasing Th (Fig. 1). In addition to the nominal LP-GRS results, Fig. 1 includes for the documented Apollo/Luna regoliths (large square symbols) results where the x-axis is from the sorted 0.5 degree (Th₂₀₀₀) LP-GRS data set, but the y-axis is from ground truth (Table 1). For low-Th sites, Fig. 1 shows a systematic discrepancy between the documented-location results and the global Th spectrum of even the most recent (Th₂₀₀₂) LP-GRS calibration. The discrepancy is largest for the most Th-poor Apollo/Luna site, Luna 24 (0.36 μ g/g: Table 2). In the 0.5 degree (Th₂₀₀₀) data set, 58.5% of the global surface has lower Th than the Luna 24 location, yet in Th₂₀₀₂, only 13.5% of the surface has Th $\leq 0.36 \, \mu g/g$.

This discrepancy is conceivably an artifact of misregistration of the LP-GRS data and/or unrepresentative sampling by the Luna probes of regions with heterogeneous regoliths. However, as indicated by the error bars in Fig. 1, the 0.5 degree LP-GRS Th results for the areas in question do not imply particularly high Th diversity. For example, Fig. 3 shows in detail the Th distribution (per Th₂₀₀₀) around the Luna 24 site. The data indicate a slight north-to-south regional gradient, but the eight cells surrounding the landing site's cell have nearly identical (within 5% relative) Th. Before addressing the consequences of this discrepancy, we next examine, using lunaites, one more manifestation of (probably) the same problem.

ORBITAL TH RESULTS VERSUS GROUND TRUTH INCLUDING LUNAITES

Lunaites and the Global Regolith Th Spectrum

We now seek to use samples to constrain the spectrum of Th concentrations in the global lunar regolith for comparison with the spectrum of concentrations in the latest LP-GRS data set, i.e., the Th₂₀₀₂ calibration of Prettyman et al. (2002) and Lawrence et al. (2003). Even though the lunaites are of unknown provenance, they can, as a population, be used for this purpose. Launch locations of lunaites may be slightly biased toward the Moon's orbit-leading (western) hemisphere (Wiesel 1971; Bandermann and Singer 1973; Pinet 1985). To the extent they are, they will be biased toward high Th (according to Lawrence et al. [2003], about 80% of the



0

2

4

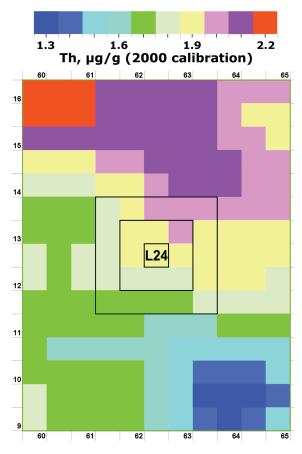


Fig. 3. Thorium concentrations in the 25 pixels closest to the Luna 24 landing site are relatively uniform in a 0.5 degree projection of the LP-GRS data (Lawrence et al. 2000).

surfaces with $>3 \mu g/g$ Th are in the western hemisphere) and also slightly biased toward maria. However, Brett Gladman (1996; personal communication) asserts that the launch site distribution is very nearly random. Assuming randomness, for a population of roughly twenty known launches, the average distance between a lunaite launch site and its nearest neighbor must be on the order of 600 km (derived by simulations using a random number function to enter sets of random latitudelongitude coordinates). If only the approximately 15 separate highland lunaite launches are considered, the average distance between a launch site and its nearest neighbor must be on the order of 800 km. For comparison, the average distance between one of the six Apollo sites and its nearest neighbor is 420 km. The Apollo sites are better sampled (multiple regolith sampling across traverses as long as 11 km). However, such intensive sampling would probably be less of an advantage, had most of these missions not specifically targeted extraordinarily heterogeneous areas such as mare/highland boundaries. For purposes of constraining the spectrum of Th concentrations in the global lunar regolith (Fig. 4), I assume that each distinct lunaite regolith breccia is comparable in importance to an average regolith composition from an individual member of the nine clustered Apollo/Luna sites.

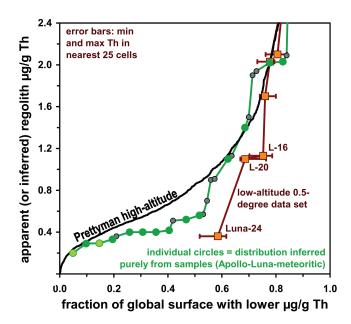


Fig. 4. Low end of the global spectrum of regolith Th concentrations plotted as a function of fractional abundance relative to the total lunar surface as calibrated by Prettyman et al. (2002); cf. Fig. 1. Shown for comparison (orange points) is the global spectrum as constrained by the Th rankings of Apollo/Luna regolith sampling sites according to low-altitude, 0.5 degree per pixel, LP-GRS data (Lawrence et al. 2000). Also shown (greens and gray) is the global spectrum as constrained by a combination of lunaites and Apollo/Luna regolith samples (Table 3). Large green circles denote highland samples; smaller gray circles denote mare samples.

A disproportionate eight of the approximately thirty lunaites-classifying Yamato- (Y-) 793274 and Queen Alexandra Range (QUE) 94281 as more mare than highland-and six out of the approximately eighteen that are not wholly regolith breccia are from mare sites. The overall surface proportion of maria is closer to 17% (Taylor 1982) or perhaps 18-19% if we include partial outcrops of buried maria, i.e., cryptomaria (Antonenko et al. 1995). Compared to ancient, impact-battered highland rocks, mare basalts are usually far fresher and tougher. This is knowledge gained in part from personal experience: "hand" crushing of mare basalt chips for chemical analysis is dreadfully hard work. Thus, even apart from the possible slight launch-site bias mentioned above, disproportionate representation of mare samples is a predictable consequence of the strength screening of lunaites noted by Warren (2001a). Incidentally, KREEP-rich basalts and impact-melt rocks may also be favored by their comparative youth, and thus, in a very general sense, limited exposure to shock effects.

In any event, we need to correct for the overabundance of mare lunaites before using average compositions of the individual lunaites as representatives of the spectrum of Th concentrations in the global lunar regolith. In fact, we need to similarly correct for bias in the Apollo/Luna sample population because for various reasons (e.g., relatively smooth landing surfaces) these missions were targeted mainly at

Table 3. Samples used for global spectrum of surface Th concentrations.

		Th
Sam	ple(s)	µg/g
Hig	hlands: 83% of surface	
1	Average of two (+) lunaite fragmental breccias ^a	0.20 ^a
	several Dhofars (e.g., 081) and Y-82192/86032	
2	ALH 81005 regolith breccia	0.29
3	Average of three lunaite impact-melt breccias ^a	0.29 ^a
	DaG 400, Dhofar 026 and NWA 482	
4	Y-791197 regolith breccia	0.33
5	MAC 88104/5 regolith breccia	0.40
6	Kalahari 008 regolith breccia ^b	0.4 ^b
7	PCA 02007 regolith breccia	0.40
8	Dar al Gani 262 regolith breccia	0.42
9	QUE 93069/94269 regolith breccia	0.52
10	Dhofar 025 regolith breccia	0.56
11	Luna 20 regolith	1.10
12	Y-793274/QUE 94281 highland component ^c	1.4°
13	Y-983885 regolith breccia	2.02
14	Apollo 16 average regolith	2.03
15	Calcalong Creek regolith breccia	4.0
16	Sayh al Uhaymir 169 regolith breccia	8.4
17	Apollo 14 average regolith	13.3
Mai	ria: 17% of surface	
1	Luna 24 regolith	0.36
2	Y-793274/QUE 94281 mare component ^c	0.51°
3	A-881757/Y-793169 mare basalt	0.57
4	Apollo 17 mare regolith	0.7
5	Dhofar 287 basalt	0.90
6	EET 87521-96008 fragmental breccia	0.91
7	Luna 16 regolith	1.13
8	Apollo 15 mare regolith	1.5
9	NWA 032 basalt	1.90
10	Apollo 11 regolith	1.94
11	NWA 773 regolith breccia	2.09
12	Apollo 12 mare regolith	3.6
a Two T	The poor samples that are arguebly regulith brassies. V 9210	2/6022 and

^aTwo Th-poor samples that are arguably regolith breccias, Y-82192/6032 and DaG 400 (see Warren et al. Forthcoming), are here conservatively regarded as fragmental breccia and impact-melt breccia, respectively.

^bThe Th datum for Kalahari 008 is an approximate value from Addi Bischoff (personal communication, 2004).

^c For the "YQ" launch-pair meteorite, the mare and highland components are based on extrapolation from mixing trends evident from many disparate analyses (Arai and Warren 1999).

Th data are averages based on all available literature data.

maria. Out of the nine sampling missions, only Apollos 14 and 16 and Luna 20 landed at dominantly highland sites. But this mare bias is easily corrected. In the extrapolation to a samplebased spectrum of Th concentration in the global lunar regolith (Fig. 4), instead of assigning equal significance to every sampling site and every lunaite, the mare and highland samples are pre-weighted as two separate components, such that the total area represented by the mare samples is 17% and the total represented by highland samples is 83%. Thus, using currently available data, with a total spectrum comprising 12 mare samples and 17 highland samples, each mare sample is assumed to represent 1.42% of the surface and each highland sample is assumed to represent 4.88%.

As representatives of the 83% of the surface assumed to be highland, I use the Apollo 14, Apollo 16, and Luna 20 regoliths along with various nonmare lunaites (Table 3). Again, the regolith breccias are more relevant for this purpose than fragmental or impact melt breccias. The model shown in Table 3 and Fig. 4 uses all of the lunaite regolith breccias (with the "YQ" launch pair regarded as a single datum; cf. Arai and Warren 1999), augmented with an average of the three lunaite impact-melt breccias and an average of the two lunaite fragmental breccias. Using these two averages for five Th-poor impact-melt and fragmental breccias effectively deemphasizes these samples in relation to the regolith samples. This is a conservative approach, considering that two of the averaged samples, "fragmental breccia" Y-82192/6032 and "impact-melt breccia" DaG 400, are arguably regolith breccias (Warren et al. Forthcoming), that fragmental breccia Dhofar 081, as discussed by Warren et al. (Forthcoming), is thoroughly polymict and likely contains a significant regolith component; and that Dhofar 026 is a unique impact-melt breccia with crystalline mafic spheroids that suggest its groundmass may have originally formed as a regolith (Warren et al. Forthcoming). The values used for the samples representing the 17% mare portion of the surface are not crucial. The emphasis in this study is the portion of the spectrum with Th concentration below 1 μ g/g.

Conventional pairing and also launch pairing, especially between young-launch-age lunaites, are potentially important complications in this connection. However, as discussed in Warren et al. (Forthcoming), a high incidence of launch pairing among the young-launch-age lunaites would have to be a statistical fluke, given that several lunaites have high launch ages and that for every high launch age there should be many recent launches (Gladman, personal communication; Gladman et al. 1996). Moreover, the many Dhofar lunaites are conservatively regarded as just three discrete samples in Table 3. Thermoluminescence results (Sutton and Crozaz 1983; Benoit et al. 1996) suggest that Allan Hills (ALH) 81005 was launched significantly earlier than Y-791197 and Dar al Gani (DaG) 262. Also, ALH 81005 has an extraordinarily high mg ratio, which makes it a very unlikely pair with ferroan regolith breccias such as DaG 262 and especially Y-791197 (Warren 1994).

Figure 4 allows comparison between the sample ground truth and the spectrum of surface Th concentration results from the LP-GRS as revised by Prettyman et al. (2002), i.e., Th₂₀₀₂. For Th less than ~1.0 μ g/g, the clear contrast between the sample-derived spectrum and the Th₂₀₀₂ spectrum represents another indication that the Th₂₀₀₂ calibration is still inaccurate-high at the low end. Note that the y-axis (Th concentration) position of the sample-derived spectrum in Fig. 4 is most firmly established, i.e., least prone to

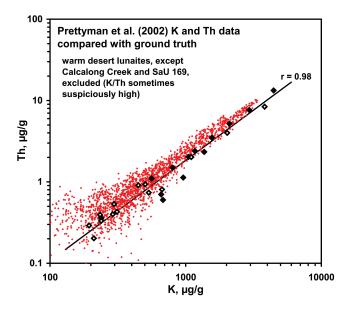


Fig. 5. On a plot of Th versus K, LP-GRS data (red; as calibrated by Prettyman et al. 2002) plot consistently to the high-Th/K side of Apollo/Luna regolith sample data (large diamonds; filled = Apollo/Luna regolith and regolith breccia samples; open = lunaites). Note that, except for Calcalong Creek and SaU 169, which, based on overall incompatible element levels undoubtedly had high (and thus relatively contamination-immune) K concentrations before leaving the Moon, lunaites of warm desert find origin (e.g., DaG 262, Dhofar 025) are excluded from the data set used for this plot.

displacement upon discovery of a few additional lunaites that do not conform well to the present trend, at about 0.5 on the xaxis, which is precisely where the discrepancy versus the Th₂₀₀₂ spectrum is most evident. Among other things, the Th₂₀₀₂ calibration implies that eight out of eleven lunaite highland regolith breccias all happen to come from the 36% of the lunar surface with Th <0.61 µg/g.

Thorium versus Potassium

Another LP-GRS calibration problem, possibly in part the same zero-offset Th problem, is manifested on a plot of K versus Th (Fig. 5), where ground truth data for lunaites and Apollo/Luna regolith samples are shown along with LP-GRS data as calibrated by Prettyman et al. (2002). Both data sets show strong correlations between K and Th. Both trends feature steadily decreasing K/Th with increasing overall KREEP level; K/Th is about 2.3 times higher in the most anorthositic regolith samples than in the KREEPiest sample (Apollo 14). But the LP-GRS data show a strong tendency to plot to the high-Th/K side of the ground truth. In the middle portion of the range (Th = $1-5 \mu g/g$) where the LP-GRS trend is most clearly defined, the axis of the LP-GRS trend has Th/ K \sim 1.2 times the regression line from the ground truth. Below Th ~1 μ g/g, the LP-GRS data show greatly increased Th/Kratio scatter, and there is a weak tendency toward even greater relative offset between the LP-GRS data and ground truth.

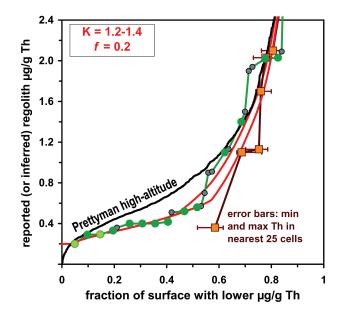


Fig. 6. Low end of the global spectrum of regolith Th concentrations, plotted as a function of fractional abundance relative to the total lunar surface as calibrated by Prettyman et al. (2002) and as implied by two variants of a proposed recalibration (Th_{rec}, red curves). Over the lowest 50% of the Th distribution, the Th_{rec} trend is set to nearly match the global spectrum as constrained by a combination of lunaites and Apollo/Luna regolith samples (green points; cf. Fig. 4). Over the intermediate portion of the Th range, the Th_{rec} trend (assuming k = 1.3) is a compromise between the green data set and the global spectrum as constrained by the Th rankings of Apollo/Luna regolith sampling sites according to low-altitude, 0.5 degree per pixel, LP-GRS data (orange points; cf. Fig. 4). At higher Th (not shown, but cf. Fig. 7), the Th_{rec} trend plots above the Prettyman et al. (2002) trend.

But in general, the trends remain nearly parallel over about a factor of ~10 in concentrations. This near-parallelism implies that a simple zero-offset for Th (of some fixed absolute magnitude, say, 0.5 μ g/g) is not the main cause of the offset between the LP-GRS K versus Th trend (Fig. 5) and ground truth. Of course, there is no guarantee that the Prettyman et al. (2002) calibration for K is more accurate than their calibration for Th. Lacking further constraints, the least prejudicial, most balanced interpretation regarding Th is to correct by a factor that would reduce the offset (Fig. 5) halfway toward the ground truth data, i.e., to assume that all of the Prettyman et al. (2002) Th data are high by a factor of ~1.10.

A PROPOSED RECALIBRATION

In view of the history of major calibration revisions for LP-GRS Th (Lawrence et al. 1999, 2000; Prettyman et al. 2002) and the apparent need for yet further revision, it seems increasingly clear that an empirical approach, based largely on ground truth, may ultimately be the best method for calibration for Th. It should be emphasized (in fairness, it probably cannot be emphasized enough) that Lawrence et al. (1999, 2000) chose to derive the calibration between count

	Lawrence et al.	Prettyman et al.	Recalibratio	100	
	(2000) calibration	(2002) calibration	(derivation:	see text ^a)	
			<i>k</i> = 1.2	<i>k</i> = 1.3	<i>k</i> = 1.4
Average global surface Th (µg/g)	2.40	1.58	1.49 ^a	1.45 ^a	1.41 ^a
Average far side surface Th	1.54	0.73	0.59	0.56	0.54
Average near side surface Th	3.26	2.43	2.40	2.35	2.27
Average South Pole Aitken (SPA) ^b surface Th	2.29	1.18	1.22	1.16	1.11
SPA-centered hemisphere concentration	1.63	0.71	0.66	0.63	0.60
Average Procellarum basin ^b surface Th	5.39	4.53	4.64	4.59	4.53
Procellarum-centered hemisphere concentration	3.25	2.47	2.39	2.34	2.30
Far side/near side concentration ratio	0.47	0.30	0.25	0.24	0.24
SPA-centered hemisphere/opposite hemisphere	0.51	0.29	0.28	0.28	0.27
SPA/Procellarum concentration ratio	0.43	0.26	0.26	0.25	0.24
Procellarum-centered hemisphere/ opposite hemisphere	2.09	3.58	4.05	4.18	4.39

Table 4. Some statistical-geochemical implications of the various potential LP-GRS calibrations.

^aAs indicated in the text and Fig. 7, at the extreme high end these recalibrations exceed Th_{2002} , thus, some of the high-end results in the nominal Th_{rec} data set are probably systematically high by a small factor. An otherwise identical calibration limiting Th_{rec} to never exceed Th_{2002} implies a "true" average global surface Th of 1.42 µg/g. Also, Th_{rec} ignores a further systematic-high bias of ~10% (including mid-range data) suggested by the offset in Fig. 5 (see text). The preferred model is shown in bold font.

^bIn these calculations, the South Pole Aitken (SPA) basin is assumed to have a diameter of 2500 km; Procellarum is regarded as a circular basin (not necessarily an impact basin) with diameter = 3200 km, centered at 24.5°N, 15°W.

rate and concentration from first principles, referring only to the processes involved in the creation and detection of lunar γ -rays without any reference to ground truth information. This philosophy, which Prettyman et al. (2002) seem to have basically upheld, has the advantage of rendering data sets completely unbiased by extraneous constraints. Additional ground truth constraints can always be consulted for possible improvement of the calibration, which is the purpose of this section. Improvement of the calibration will result in a better estimate for the average global surface composition and more accurate measures of compositional diversity across the surface.

The goal is to improve upon the Prettyman et al. (2002) Th calibration Th_{2002} by bringing the low-end data most of the way down toward the global concentration spectrum suggested by ground truth while retaining essentially Th_{2002} results for the higher Th concentrations. Great precision is not a goal here because the ground truth target is not precisely defined; the documented-locations data set (Fig. 1) suggests lower concentrations than the location-independent data set (Fig. 4). For convenience, the starting point is taken as the Th_{2000} 0.5 degree data set. By trial and error, I found that a data set with the desired characteristics (at the low end, intermediate between Th_{2002} and ground truth, but with increasing Th gradually overtaking Th_{2002} , such that the extreme high end is slightly higher Th than Th_{2002} , so as to better match Apollo 14) can be obtained using:

$$Th_{rec} = maximum(0.2, [Th_{2000}]^{1.5}/4, fTh_{2000} + (1))$$
$$(1-f)(Th_{14} + k)(Th_{2000}/Th_{14}) - k)$$

where Th_{rec} is the recalibrated Th concentration, f is an arbitrary constant ≈ 0.2 , Th_{14} is the Th_{2000} result for the

Apollo 14 site (11.626 $\mu g/g$), and k is another arbitrary constant ≈ 1.3 . It should be emphasized that the above equation has no theoretical foundation. It is merely a convenient, arbitrary tool for deriving the desired intermediacy between Th₂₀₀₂ and the Th spectrum suggested by ground truth. The effect of this transformation, for two values of k that straddle the nominal value of 1.3, is illustrated in Fig. 6. For the first ~50% of the Th-sorted global surface, the Th_{rec} distribution closely matches the locationindependent ground truth data set (filled circles in Figs. 4 and 6). Beyond 50% (Th ~ 0.6 μ g/g), the Th_{rec} distribution falls roughly along the average of the location-independent data set and the documented-location data set (filled squares). For k = 1.3, the Th_{rec} results begin to exceed Th₂₀₀₂ at 4.0 µg/g. At higher Th levels, the increment between Th_{2002} and Th_{rec} gradually widens and reaches a maximum of 2.7 µg/g at the highest-Th cell in the global distribution (Th_{rec} = $12.8 \ \mu g/g$). A plot analogous to Fig. 2 but with Three as the x-axis would show a ground truth = 0 intercept of ~0.44 μ g/g; thus, Th_{rec} represents only a partial, compromise fix for the problem evident in Fig. 2. The relationship between Th_{rec} and previous calibrations is further illustrated in Fig. 7.

Implications

Some direct implications from this proposed revision of the LP-GRS Th calibration are summarized in Table 4. Even though over most of the thorium range $Th_{rec} > Th_{2002}$, most of the Moon's surface is in the low-Th domain where $Th_{rec} < Th_{2002}$ (Fig. 7). The average global surface Th content is lower in Th_{rec} (1.45 µg/g) than in Th_{2002} (1.58 µg/g). Yet for estimating the average global surface Th, Th_{rec} is conservative in two respects. First, the only rationale for

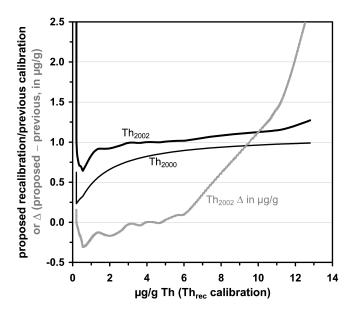


Fig. 7. Adjustment factors implied by the recommended LP-GRS Th recalibration (Th_{rec}, k = 1.3) relative to the 0.5 degree calibration of Lawrence et al. (2000) and to the 2 degree Prettyman et al. (2002) calibration. Note that the 21% of the range where the Th_{rec}/Th₂₀₀₂ ratio is less than unity (i.e., $0.21 < Th_{rec} < 3 \mu g/g$) accounts for 80% of the Moon's surface.

allowing the Th_{rec} calibration to include values greater than Th₂₀₀₂ is to improve the extreme high-end agreement with Apollo 14. But as discussed above, the poor fit between Th_{2002.5} (the 0.5 degree translation of Th₂₀₀₂) and Apollo 14 may be a strictly local artifact of the low (5 degree) spatial resolution of Th₂₀₀₂, which is inadequate to resolve the major sub-100 km scale Th variations (Lawrence et al. 2003) near the Apollo 14 site. A calibration identical to Th_{rec} except limiting Th_{true} to never exceed Th₂₀₀₂, implies a slightly lower average global surface Th of 1.42 μ g/g. Second, as discussed above, the offset between the Prettyman et al. (2002) LP-GRS K versus Th trend and ground truth (Fig. 5) suggests a systematic error by a factor of 1.1 ± 0.1 in the Th₂₀₀₂ Th data. Very conservatively assuming that only one-quarter of the offset stems from Th, the average global surface Th is implied to be ~1.35 μ g/g. For comparison, an average of 1.3 μ g/g was estimated by Metzger et al. (1977) based on extrapolation from Apollo GRS data for ~20% of the surface. Also, using the "empirical" calibration of Gillis et al. (2000), which was based on comparison between LP-GRS count rate data and Apollo sample data (i.e., a recalibration based entirely on a plot analogous to Fig. 2), Jolliff et al. (2000) derived global surface averages of $1.1-1.3 \ \mu g/g$ (the range reflects a discrepancy between their Tables 1-2).

Interpretation of Lunar Prospector Results for Other Elements

Elphic et al. (2000a, 2000b) have used the Lunar Prospector neutron spectrometer results to develop global maps of neutron-absorptive rare earth elements (Sm and Gd) and to help constrain the mapping of Fe and Ti. According to Elphic et al. (2000a), their approach was to "use GRS estimates of thorium to calculate the REE contribution to absorption." Elphic et al. (2000b) did not explain their data reduction procedure in quite the same way, but both Elphic et al. (2000a) and Elphic et al. (2000b) show an interesting plot of $\Sigma_{\rm eff}$ (regolith thermal neutron cross-section, estimated from LP neutron results) versus LP-GRS Th data from Lawrence et al. (2000). The expected trend on this plot is a straightforward positive correlation. What the plot (Elphic et al. 2000b, Plate 6) actually shows is a complicated distribution, where the comparative few pixels with Th_{2000} < 1 $\mu g/g$ or > 4 $\mu g/g$ plot in the expected regions, but pixels with $1 < Th_{2000} < 4 \mu g/g$, and especially those with $Th_{2000} \sim 2 \mu g/g$, tend to plot to the high-Th side of the expected (and to zeroeth approximation observed) trend. This otherwise enigmatic distribution appears less surprising if one considers the variation of the proposed recalibration factors for the LP-GRS Th data as a function of Th_{rec} (Fig. 7). The recalibration factors precipitously increase in severity as Th₂₀₀₀ increases from 0 to ~1.4 μ g/g (Th_{rec} increases from 0.2 to just 0.3 μ g/g), and then decay back toward unity as Th₂₀₀₀ increases from 1.4 to $3 \mu g/g$ (Th_{rec} increases from 0.3 to $3 \mu g/g$). This spike in the recalibration factor severity approximately coincides with the region of anomalously high Th/ Σ_{eff} ratio on Plate 6 of Elphic et al. (2000b). Several other enigmatic aspects of the LP neutron results, which involve very complex interrelationships among the various neutron-absorptive elements (see Elphic et al. 2000b), might become less enigmatic if recalibrated Th data are factored into the data reduction procedure.

Global Asymmetry

As summarized in Table 4, the Moon's remarkable hemispheric asymmetry in KREEP abundance is even more pronounced than seemed the case just a few years ago. For example, the surface Th concentration ratio between the hemisphere antipodal to Procellarum and the hemisphere centered on Procellarum was 0.48 in the Lawrence et al. (2000) calibration; in the Three calibration it has been reduced to 0.24. The anomalous high-Th region is obviously associated with the Procellarum basin (Lawrence et al. 2003, Fig. 12). Calling this important region by the neutral term "terrane" (the "Procellarum-KREEP terrane" of Jolliff et al. 2000 and Haskin et al. 2000) tends to obscure the salient fact that it is a basin. "Terrane" is arguably even worse than neutral, because in older lunar literature "terra" was widely used to designate the high-standing "continental" or "upland" portion of the Moon's crust. The Procellarum basin is unusually old and so heavily overprinted with later cratering that its absolute age and even the most basic issue of its origin, impact or otherwise, are impossible to determine. Some photogeologists, originally including Cadogan (1974) and notably Wilhelms (1987), but not Spudis (1993), favor impact. Citing the lack of a "central high" in the depth-tomoho distribution, geophysicists Neuman et al. (1996) argued for origin by "differentiation due to large-scale internal convection." In any event, the giant KREEP anomaly is clearly linked with a roughly circular region (with a diameter of approximately 3000 km) (Hood and Zuber 2000) of consistently low topography, high gravity, and thin crust: Procellarum basin.

As noted by Warren and Kallemeyn (1998), a large disparity in KREEP content between the two great (and nearly antipodal) lunar basins, Procellarum and South Pole Aitken, is most simply interpreted as a consequence of the more extreme antiquity of Procellarum. As the Moon transitioned from its magmasphere stage to its near-final state, the KREEP component probably became concentrated to a thin layer of residual melt or mush near the base of the crust. If during this transitional stage the first giant basin formed (i.e., Procellarum; whether by impact or not is of no great importance for this discussion), the buoyant residual melt (i.e., KREEP) probably became concentrated below that zone of thinned crust. If so, then before the second giant basin (South Pole Aitken) formed, KREEP had largely bled away from its hemisphere. The hemispheric asymmetry, which now appears even more extreme, is very difficult to explain by any model other than Warren and Kallemeyn's (1998) magmasphere-in-transition scenario.

BULK COMPOSITION OF THE MOON

The focus of discussion concerning the bulk composition of the Moon is usually a comparison to the mantle + crust portion of the Earth (also known as Earth's "primitive mantle"). Isotopic results for oxygen (Clayton and Mayeda 1996) and Cr (Lugmair and Shukolyukov 1998; Birck et al. 1999) suggest a strong kinship between the Moon and terrestrial matter. Most models of the Moon's origin assume it is the byproduct of a giant impact involving the Earth as a major contributor to the orbiting debris that eventually forms the Moon (e.g., Canup and Asphaug 2001). The obvious geochemical advantage of the giant impact model is that the Moon tends to form with an extreme depletion in core (FeNi-FeS) material, as the orbiting impact-debris derives preferentially from the peripheral portions of the impacting bodies. In some variants of the giant impact scenario, the Moon is predicted to nonetheless have a grossly different oxide-portion bulk composition enriched in refractory lithophile elements (including Th and the major elements Al and Ca) because vaporizationcondensation processes are assumed to operate during the evolution of the orbiting debris (e.g., the original model of Cameron and Ward 1976).

Crustal Th

An obvious application of global lunar surface composition data is to extrapolate from the surface composition to the bulk crust and from the bulk crust to the bulk Moon (Table 5). For example, Taylor (1982) and Drake (1986) assumed that the estimated surface composition is representative of the bulk crust and that the crust is 12 wt% of the Moon (the less than bulk density of the crust was ignored and its thickness was assumed to be 73 km). These extrapolations implied a bulk Moon composition significantly enriched in Th and other refractory lithophile elements in comparison to the Earth's primitive mantle, mainly because the crust was assumed to constitute such a large weight fraction of the Moon. Recent modeling of the lunar seismic database using an improved inverse Monte Carlo technique indicates that the crustal thickness is actually only about 38 ± 3 km in the central nearside Apollo region (Khan et al. 2000; Khan and Mosegaard 2002). Lognonné et al. (2003) independently modeled the lunar seismic database and derived an even lower crustal thickness for the Apollo region of 30 ± 3 km. However, Wieczorek (2003) has argued that 30 km is only "marginally consistent" with broader geophysical constraints.

For extrapolation from the Apollo region to a global average crustal thickness, it is customary to assume the topographically higher farside crust is roughly 1.5 times thicker, and thus the global average is about 1.2–1.3 times thicker (e.g., BVSP 1981; Taylor 1982). The implied global average crustal thickness is about 45–50 km, approximately two-thirds as thick as assumed in most past extrapolations from surface composition to bulk Moon composition.

As discussed above, a conservatively high estimate for the average global surface Th concentration is ~1.35 μ g/g. To extrapolate from the average surface to an average crust composition, some further adjustments are needed. Warren (2001b) found that the deeper crust is depleted in Th compared to the surface, based on LP-GRS Th results from in and around large craters. The deepest ejecta of these structures are presumably concentrated within and shortly outside their rims; the data reveal a strong inverse correlation between crater diameter and crater/background Th concentration ratio. The indicated compensation factor for converting from surface Th concentration to average underlying crust Th concentration, could be anywhere from 0.3 to 0.76, depending on the weight given to the result from one outstandingly large crater: Orientale basin.

Orientale is exceptionally young. All other craters larger than 300 km in diameter are too altered by subsequent cratering and magmatism to be useful in this type of study, and even Orientale is altered to some extent (e.g., its interior is partly covered with mare basalt). Giving reduced emphasis to Orientale, yet not ignoring it, suggests a compensation factor of ~0.6.

If surface Th concentration is to be assumed to be proportional to the underlying crust's Th, an additional compensation factor is required by the anticorrelation between surface Th and crustal thickness (Metzger et al. 1977; Lawrence et al. 2000). By weighting each Th_{2000} pixel in proportion to crustal thickness (Neumann et al. 1996),

ZoneModelModel-defining assumptionCrustAsurface = bulk crustBsurface = bulk crustCsurface = enriched crust ^a Csurface = enriched crust ^a Recommended: thin-crust areas = enriched X1: same, except for crustal thicknessX2: same, except for crustal thicknessJJolliff et al. (2000)MantleAsurface = bulk crustBsurface = bulk crustCenriched crust	Model-defining assumptions surface = bulk crust surface = bulk crust							
C B A J Recon C B A	ulk crust ulk crust	calibration	(km)	(kg m ⁻³)	(% of total)	(g/gh)	(β/g)	(%)
Recon C B	ulk crust miched crust	Th_{2002}	48	2900	7.0	1.58	0.110	83
C Recon	nrichad cructa	$\mathrm{Th}_{\mathrm{rec}}$	48	2900	7.0	1.35	0.094	80
Recon B A J B B	TILICITCU CLUST	$\mathrm{Th}_{\mathrm{rec}}$	48	2900	7.0	0.81	0.057	71
r ∠ a c	reas = enriched ^b	Th_{rec}	48	2900	7.0	0.71	0.050	68
μΑ Υ Γ	crustal thickness				5.6	0.57	0.040	63
ה ע מ נ	crustal thickness				8.7	0.88	0.062	73
≺ a (. (2000)	Jolliff	70	2920	10.2	1.05	0.107	75
B $surface = bu$	ulk crust		1390	3360	91.8	0.025	0.023	17
	ulk crust		1390	3360	91.8	0.025	0.023	20
	surface = enriched crust ^a		1390	3360	91.8	0.025	0.023	29
Recommended: thin-crust areas = enriched ^b	reas = enriched ^b		1390	3360	91.8	0.025	0.023	32
X1: same, except for crustal thickness	ustal thickness				93.2	0.025	0.023	37
X2: same, except for crustal thickness	ustal thickness				90.1	0.025	0.023	27
J Jolliff et al. (2000)	. (2000)		1368	3390	89.1	0.04	0.036	25
Core A-X (metal and sulfide)	sulfide)		300	8000	1.23	0	0	0
A surface = bulk crust	ulk crust		1738	3344	100.0	0.133		
B surface = bulk crust	ulk crust					0.117		
C surface = en	surface = enriched crust ^a					0.080		
Recommended: thin-crust areas = enriched ^b	$reas = enriched^b$					0.073		
X1: same, except for crustal thickness	ustal thickness					0.063		
X2: same, except for crustal thickness	ustal thickness					0.084		
J Jolliff et al. (2000)	. (2000)					0.142		
For comparison, Earth's primitive mantle ^c	ntle ^c					0.077		

Table 5. Simple mass balance models for lunar thorium.

composition. ^cTh concentration shown for Earth's primitive mantle is an average of estimates of 0.070 μg/g by Taylor (1982), 0.0813 (sic) μg/g by Hofmann (1988), and 0.0795 (sic) μg/g by McDonough and Sun (1995).

Warren (2001b) found a value of 0.917 for this compensation factor. Substituting the Th_{rec} recalibration, the factor becomes 0.88. The compounded compensation factor for extrapolation of bulk crustal Th from surface Th is thus $0.6 \times 0.88 = 0.53$. This is not much different than a factor derived in earlier work (before data of sufficient precision and spatial resolution were available to assess the depth versus surface compositional contrast) based on division of the surface into geological terrains, namely Metzger et al. (1977). Metzger et al. (1977) used a factor of 0.62 in converting from their estimate for global surface Th (1.3 μ g/g) to one for bulk crustal Th $(0.8 \,\mu\text{g/g})$. However, the analogous factor derived using a "terrain" method by Jolliff et al. (2000) was 0.82-0.95 (the range reflects discrepancy between their Tables 1 and 2). Applying corrections for both effects (depth-linked heterogeneity and crustal thickness) results in an average crustal Th concentration of ~0.71 μ g/g. This estimate is probably conservatively high, because the compensation factor for depth-linked heterogeneity (assumed = 0.6) has a larger uncertainty downward (toward 0.3) than upward (toward 0.76) (Warren 2001b).

Mantle Th

Jolliff et al. (2000) argued for a mantle Th concentration of 0.04 μ g/g. However, in view of the bulk crustal Th concentration inferred above, 0.04 μ g/g in the mantle would imply, for the range of bulk crustal Th shown in Table 5, that the crust/mantle partition coefficient for Th is only 15–22 (the corresponding value for the Earth is roughly 200) (Sun and McDonough 1989), and that 37–48% of the Moon's Th failed to differentiate into the crust. Such an incomplete differentiation seems hard to reconcile with the generally accepted view that the lunar mantle was at one time so extensively molten that it resembled a magma ocean.

No lunar mantle xenoliths are available, but a great variety of mantle-derived mare basalts have been sampled. An advantage of Th is that it is thoroughly incompatible, even with high-pressure minerals that might otherwise lessen the value of analogy to terrestrial basalts (e.g., Hirschmann and Stolper 1996). Mid-ocean ridge basalt (MORB), with Th concentrations of typically 0.2–0.3 µg/g (Hofmann 1988; Sun and McDonough. 1989), is believed to originate from highly depleted mantle, for which a conservatively high estimate (Hirschmann and Stolper 1996) has Th ~0.02 µg/g. DePaolo's (1988) estimate was $\sim 0.012 \,\mu$ g/g. Thus, MORBs are enriched in Th by a factor of roughly 10-20 versus their source regions. For comparison, the average Th concentration in mare basalt is ~1.1 μ g/g (Arai and Warren 1999), and mare volcanic glasses have on average roughly 0.5 times lower Th in particular and incompatible elements in general than the sampled mare basalts (Shearer and Papike 1999; Korotev 1998). Of course, MORB forms as a byproduct of plate tectonics, a uniquely terrestrial phenomenon. Another

complication is that some of the higher mare-basaltic Th concentrations may reflect assimilation of crustal KREEP (Binder 1982).

A more direct analogy is to ocean-island basalts, which are believed to originate from deep plumes in undepleted mantle and which on average contain about 4 μ g/g Th (Sun and McDonough 1989), roughly four times the average mare basalt level and eight times the average mare volcanic glass level. The ocean-island basalt source regions are generally assumed to approximate primitive mantle, the Th concentration of which is estimated with incredible consistency to be 0.075 ± 0.006 μ g/g (Table 5). Thus, oceanisland basalts appear to be enriched in Th by a factor of roughly 50 versus their source regions.

The ocean-island basalt analogy implies the mare source regions held roughly 0.01-0.03 µg/g Th, and the far less direct MORB analogy suggests roughly 0.03-0.10 µg/g. However, it is quite a different matter to extrapolate further from the mare sources to the bulk lunar mantle. It must be borne in mind that the total volume of mare basalt is comparatively tiny; e.g., as estimated by Hörz (1978), only 0.005-0.009 vol% of the Moon. Even with a conservative estimate for the average degree of melting, say 2%, and even assuming the exposed extrusives are only a small fraction, say 1/4, of the total volume of mare-related magma emplaced within the crust, Hörz's (1978) estimate implies that only about 2% of the total mantle volume was directly involved in mare-related magmatism. In the terrestrial mantle, partial melting occurs at locales determined by plate tectonic motions and is almost indiscriminate with respect to composition. In contrast, the lunar mantle has not been well stirred (as shown by humongous isotopic heterogeneities, e.g., Beard et al. 1998) since its origin as a mass of sunken cumulates in the primordial magmasphere. Melting in such a material is probably not at all indiscriminate with respect to composition. Regions relatively rich in Th, U, and K (heat sources and incompatible elements that tend to track with low-temperature-melting components) must be favored locales for partial melting. Thus, the 0.03 µg/g Th inferred from the ocean-island basalt analogy is probably best viewed as a severe upper limit on the bulk mantle Th concentration. I adopt a round number of 0.025 $\mu g/g$ as an estimated lunar mantle Th concentration.

Bulk Moon: Refractory Lithophile Elements

The Moon's small core (Konopliv et al. 1998) presumably contains negligible Th, so an estimate for the bulk Moon Th concentration is easily calculated from estimates for crust and mantle composition combined with an estimated crustal thickness and density (Table 5). The estimated bulk Moon Th concentration, ~0.073 μ g/g, is marginally consistent with an estimate constrained by heat flow data: 0.049–0.074 μ g/g (Warren and Rasmussen 1987; their estimated U concentration

is here converted into Th, assuming chondritic Th/U). Bearing in mind that both the Th_{rec} recalibration and the assumed 45– 50 km crustal thickness are probably conservatively high and that the crust (by the Table 5 model) contains 70% of the Moon's total Th budget, 0.07 μ g/g appears a conservatively high final estimate for bulk Moon Th.

Without introducing biases from assumptions about how the Moon formed, the simplest general assumption about its bulk composition is that it resembles chondritic meteorites (which, almost by definition, are compositionally close to the mean solar system, minus, in varying degrees, volatile constituents), except for the obvious lunar depletions in reduced (FeNi-metal and sulfide) and volatile components. The chondritic model has been applied to estimation of Earth's primitive mantle composition (e.g., most explicitly, Hart and Zindler 1986; McDonough and Sun 1995) in excellent agreement with the consensus from all approaches to the problem (Table 6).

Absent strong evidence to the contrary, I assume that all refractory lithophile elements are in chondritic proportion to the best constrained of the group, Th; where refractory lithophile refers to the 29 lithophile elements that have solar nebula condensation temperatures (Wasson 1985) higher than that of Mg, i.e., Al, Ca, Sc, Ti, Sr, Y, Zr, Nb, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Th, and U, and also the strictly radioactive elements Ra and Ac. Normally, the refractory element V would also be considered lithophile. However, Ringwood et al. (1990) argued that V may be siderophile at the extremely high pressures of the Earth's lower mantle and core, conditions that could be relevant if (although only if) the Moon originated largely from terrestrial material.

Incidentally, a common and persistent misconception notwithstanding, the Moon's gross depletion in volatile elements has no obvious bearing on its major-element composition. After Mg, the next most refractory major element is Si. Total depletion of every constituent with volatility (i.e., solar nebula condensation temperature; Wasson 1985) between that of Si and the most volatile of all (H₂O), from even the most volatile-rich (CI) type of chondrite, would increase the concentrations of all elements more refractory than Si by a factor of 1.22. However, for ten other types of chondrites analyzed by Jarosewich (1990), the increase would be merely a factor of 1.02-1.09 (average 1.05), an "enrichment" that, in a bulk planet, must be hard to detect. Of course, with the right time-temperature sequence, it might be possible to selectively deplete major elements to some extent as well, but in such a scenario the intermediatevolatility lithophile species Cr₂O₃ and MnO, especially the latter, would be expected to show strong depletions relative to MgO. We can see this effect in the bulk Earth. By all accounts, Cr₂O₃/MgO and especially MnO/MgO are less than chondritic in the Earth's primitive mantle. The estimated Earth's primitive mantle composition of Taylor (1982) is very

typical; relative to CI, it has $Cr_2O_3/MgO = 0.46$ and MnO/MgO = 0.21. On the contrary, models invoking a refractoryenriched bulk Moon generally imply (as a byproduct of relatively low MgO content) Cr_2O_3/MgO and MnO/MgO being higher in the Moon than in the Earth's primitive mantle. For example, Taylor's (1982, 1999) estimated bulk Moon features, relative to CI, $Cr_2O_3/MgO = 0.76$ and MnO/MgO = 0.30.

For the 27 stable refractory lithophile elements, the term "chondritic proportion" has quite specific connotations. For nine highly diverse chondrite types studied by Wasson and Kallemeyn (1988), the element/Th ratio is a constant to within 9% (1 σ ; ignoring scatter in some of the less well-determined middle REE that presumably is more analytical than real) for all but four of the 27, and to within 12% for all but one of the 27. The major exception is Zr ($\sigma = 14\%$), where again, analytical problems may be the main reason (the Zr/Th result for CM chondrites is aberrant). Even for Mg/Th, the element/Th ratio is a constant to within 13%.

The resultant extrapolations are shown in Table 6. It is interesting to assess what proportion of the implied bulk Moon Al_2O_3 content (3.8 wt%) is present within the crust. Based on many highland regolith samples (e.g., Warren et al. Forthcoming), the average highland surface Al₂O₃ content is estimated to be 28.5 wt% (Korotev et al. 2003). This is probably unrepresentatively high compared to the full crustal depth range. Khan et al. (2000) found markedly higher seismic velocities in the crust below about 15 km, suggesting higher mafic content, and lower Al₂O₃. Taking the 25 wt% value as a conservative estimate of the bulk crust composition and assuming the crustal thickness is \sim 45–50 km (see above), the amount of Al₂O₃ in the crust expressed as bulk Moon Al₂O₃ is implied to be 1.75 wt%. Thus, the estimated refractory lithophile levels appear conservative, inasmuch as they imply that less than half of the Moon's Al₂O₃ managed to differentiate into its crust, despite the fact that buoyant plagioclase is the only stable host for Al₂O₃ in most of the volume of this relatively small body that by common estimation underwent very extensive primordial melting. This model leaves an average Al₂O₃ concentration of 2.3 wt% in the lunar mantle, consistent with recent evidence for garnet fractionation in the derivation of some mare basalts (Beard et al. 1998; Neal 2001), and with a high density (hinting at garnet) in the deepest lunar mantle (Khan et al. 2001). Assuming (merely as the simplest possible model) the concentration of Al₂O₃ in the mantle is independent of depth, 2.3 wt% would translate into 7 wt% plagioclase in the upper mantle, where garnet is unstable.

Bulk Moon: Major Elements

Having estimated Al, Ca, Ti, and so forth, only four major elements remain: O, Mg, Si, and Fe. For the 99 wt% of the Moon that is above its core, the total of $(MgO + SiO_2 +$

	Th ng/g	Na ₂ O wt%	MgO wt%	Al ₂ O ₃ wt%	SiO ₂ wt%	$ m K_2O$ wt%	CaO wt%	TiO ₂ wt%	Cr ₂ O ₃ wt%	MnO wt%	FeO wt%	Mg mol%
CI chondrites ^a	29	0.661	16.08	1.62	22.46	0.067	1.29	0.070	0.387	0.245	17.0^{a}	
Preferred model, $Mg/Si = 1.10 \times CI$	70	0.050	35.6	3.82	46.2	0.005	3.02	0.18	0.44	0.130	9.12	87.4
Same, excluding 1.2 wt% core	71	0.051	36.0	3.87	46.8	0.005	3.06	0.18	0.44	0.132	9.24	87.4
Alternative models, excluding core 1. Th (including core) = 65 مو/ه	99	0.051	36.2	3 60	47.0	0.005	2.85	0 17	0 44	0.133	9.29	87.4
2, $Mg/Si = 1.03 \times CI$	71	0.051	34.8	3.87	48.3	0.005	3.06	0.18	0.44	0.127	8.92	87.4
$3, Mg/Si = 1.17 \times CI$	71	0.051	37.2	3.87	45.3	0.005	3.06	0.18	0.44	0.136	9.53	87.4
4, $MgO/FeO = 4.4$	71	0.051	36.4	3.87	47.3	0.005	3.06	0.18	0.44	0.118	8.28	88.7
5, $MgO/FeO = 3.4$	71	0.051	35.5	3.87	46.1	0.005	3.06	0.18	0.44	0.149	10.44	85.8
Previous lunar bulk noncore composition models	n models											
Taylor (1999)	114	0.09	32.0	6.0	43.4	0.010	4.5	0.30	0.61	0.15	13.0	81.4
O'Neill (1991)	68	0.04	35.1	3.9	44.6	0.004	3.3	0.19	0.46	0.17	12.4	83.5
Ringwood et al. (1987)	pu	0.06	36.9	3.72	43.2	pu	3.03	0.30	0.32	0.16	12.24	84.3
Jones and Delano (1986)	pu	nd	37.1	3.7	42.6	nd	3.0	0.19	nd	0.19	13.6	82.9
Wänke and Dreibus (1982)	72	0.057	35.5	3.76	44.3	0.005	3.15	0.18	0.37	0.16	12.65	83.3
Buck and Toksöz (1980)	nd	0.15	29.0	5.00	48.4	pu	3.83	0.40	0.30	pu	12.90	80.0
Ringwood (1979)	pu	0.05	32.7	4.2	44.8	nd	3.7	0.3	0.4	pu	13.9	80.7
Morgan et al. (1978)	145	0.097	29.1	7.58	43.3	0.009	6.13	0.39	0.30	0.15	12.96	80.0
For comparison: literature estimates for bulk composition of	bulk con	e	Earth's prin	Earth's primitive mantle (EPM)	(EPM)							
Anderson (1983)	LL LL	0.275	34.0	3.82	47.9	0.018	3.08	0.204	0.342	0.131	7.86	88.5
Taylor and McLennan (1985)	64	0.340	35.1	3.64	49.9	0.020	2.89	0.160	0.438	0.129	8.00	88.7
Hart and Zindler (1986)	75	0.292	35.7	3.56	49.5	0.028	2.82	0.159	0.412	0.115	7.14	89.9
Wänke and Dreibus (1988)	76	0.390	36.9	4.20	45.9	0.028	3.54	0.230	0.440	0.130	7.58	89.7
Hofmann (1988)	81	0.332	37.8	4.06	46.0	0.031	3.21	0.181	nd	pu	7.54	89.9
Allegre et al. (1995)	pu	0.360	37.8	4.09	46.1	0.034	3.23	0.180	0.38	0.149	7.49	90.0
McDonough and Sun (1995)	80	0.360	37.8	4.45	45.0	0.029	3.55	0.201	0.384	0.135	8.05	89.3
Consensus average EPM	75	0.34	36.4	3.97	47.2	0.027	3.19	0.188	0.40	0.132	7.67	89.4
± (one-sigma)	9	0.04	1.4	0.29	1.8	0.005	0.27	0.024	0.03	0.010	0.30	0.6

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Table 6. Continued. Estimated bulk composition of t	k compo	sition of	the Mod	on, and f	or comp:	arison, li	terature e	stimates	for the N	Aoon and	for the E	he Moon, and for comparison, literature estimates for the Moon and for the Earth's primitive mantle.	nitive m	antle.
	\mathbf{Sc}	>	Ga	\mathbf{Sr}	Y	Zr	ЧN	Ba	La	Lu	Hf	Та	D	Sum
	μg/g	μg/g	µg/g	μg/g	µg/g	µg∕g	μg/g	µg/g	µg/g	µg/g	µg/g	µg/g	ng/g	wt%
CI chondrites ^a	5.8	55	9.8	7.9	1.44	3.8	0.27	2.3	0.236	0.025	0.12	0.016	8.2	59.9
Preferred model, $Mg/Si = 1.10 \times CI$	14.0	100	0.50	19.1	3.5	9.2	0.65	5.6	0.57	0.059	0.29	0.039	20	98.5
same, excluding 1.2 wt% core	14.2	101	0.51	19.3	3.5	9.3	0.66	5.6	0.58	090.0	0.29	0.039	20	8.66
Alternative models, excluding core														
1, Th (including core) = 65 ng/g	13.2	101	0.51	17.9	3.3	8.6	0.61	5.2	0.54	0.056	0.27	0.036	19	99.8
2, $Mg/Si = 1.03 \times CI$	14.2	101	0.51	19.3	3.5	9.3	0.66	5.6	0.58	0.060	0.29	0.039	20	99.8
3, $Mg/Si = 1.17 \times CI$	14.2	101	0.51	19.3	3.5	9.3	0.66	5.6	0.58	0.060	0.29	0.039	20	99.8
4, $MgO/FeO = 4.4$	14.2	101	0.51	19.3	3.5	9.3	0.66	5.6	0.58	0.060	0.29	0.039	20	99.8
5, $MgO/FeO = 3.4$	14.2	101	0.51	19.3	3.5	9.3	0.66	5.6	0.58	0.060	0.29	0.039	20	99.8
Previous lunar bulk noncore composition models	ion model	S												
Taylor (1999)	19	150	pu	30	5.1	14	1.1	8.8	0.90	0.093	0.42	pu	30	100.1
O'Neill (1991)	15.4	81	0.24	pu	pu	pu	pu	pu	pu	pu	pu	nd	19	100.2
Ringwood et al. (1987)	14	79	pu	pu	pu	pu	pu	pu	pu	pu	pu	pu	pu	6.66
Jones and Delano (1986)	pu	pu	pu	pu	pu	pu	pu	pu	pu	pu	pu	pu	pu	100.4
Wänke and Dreibus (1982)	14.3	74	pu	21	pu	pu	pu	5.1	0.59	nd	nd	nd	20	100.1
Buck and Toksöz (1980)	pu	pu	pu	pu	pu	pu	pu	pu	pu	nd	pu	nd	pu	100.0
Ringwood (1979)	pu	pu	pu	pu	pu	pu	pu	pu	pu	pu	pu	pu	pu	100.1
Morgan et al. (1978)	27.6	235	0.62	41.8	7.6	45	2.24	11.6	1.08	0.110	0.65	0.066	41	100.0
For comparison: literature estimates for bulk composition o	or bulk co	mposition		s primitive	f Earth's primitive mantle (EPM)	EPM).								
Anderson (1983)	15	77	4.0	16.2	3.26	13	0.97	5.22	0.57	0.06	0.33	0.04	19.6	97.7
Taylor and McLennan (1985)	13	128	3.0	17.8	3.4	17.8	0.56	5.1	0.55	0.057	0.27	0.04	18	100.6
Hart and Zindler (1986)	pu	pu	pu	19.6	pu	pu	pu	pu	pu	pu	pu	pu	20.8	7.66
Wänke and Dreibus (1988)	17.0	82.1	3.8	27.7	pu	pu	nd	5.60	0.52	0.074	0.28	0.026	21	99.3
Hofmann (1988)	14.9	pu	pu	18.2	3.94	9.7	0.62	6.05	0.61	0.064	0.268	0.035	20.3	99.1
Allegre et al. (1995)	pu	pu	pu	pu	pu	pu	pu	nd	pu	pu	nd	pu	pu	8.66
McDonough and Sun (1995)	16.2	82	4.0	19.9	4.30	10.5	0.66	9.9	0.65	0.068	0.283	0.037	20.3	100.0
Consensus average EPM	15.2	92	3.7	20	3.7	12.8	0.70	5.7	0.58	0.064	0.286	0.036	20.0	99.5
± (one-sigma)	1.4	21	0.4	4	0.4	3.2	0.16	0.6	0.05	0.006	0.023	0.005	1.0	
^a CI chondrites average composition is from Wasson and Kallemeyn (1988). However, total FeO + The preferred model and key parameters that define the alternative models are shown in bold type	Wasson and define the	l Kallemeyı alternative	n (1988). H models are	owever, to	tal FeO + F bold type.	e2O3 is esti	mated from	Jarosewich	(1990) and	(1988). However, total FeO + Fe_2O_3 is estimated from Jarosewich (1990) and reported here as FeO nodels are shown in bold type.	re as FeO.			
nd = not determined.														

FeO) is constrained by the difference between 100 and (Al₂O₃ + CaO + TiO₂ + about 1% for all other oxides). Of these, FeO is the most idiosyncratic. Among chondrites, FeO varies from virtually zero in enstatite types, to ~30 wt% in some of the more oxidized types; analogy with the Earth's mantle FeO concentration is also of dubious value, because on grounds of simple density contrast, total Fe (i.e., FeO plus Fe in reduced species, FeNi and FeS) is vastly different between the Earth and its Moon. However, to fix the major element composition, it will be sufficient to estimate MgO/FeO (i.e., the oxide mg) and any one of MgO, FeO, or SiO₂, or for oxide mg and MgO/SiO₂ (or even, in principle, FeO/SiO₂) and all of the remaining major oxide concentrations are implicitly fixed.

The least volatile of these three unfixed major oxides is MgO. Among the nine chondrite types of Wasson and Kallemeyn (1988), Mg/Th is constant to within 13% (1 σ). For a CI-chondritic Mg/Th ratio, the implied bulk Moon MgO would be 39 wt%. This should be considered a provisional result, subject to modest revision (downward, assuming MgO/Th fractionation would be governed by volatility relationships) after estimation of the mg and MgO/SiO₂ ratios.

Oxide mg, Estimated from Seismology

In most previous estimations of the bulk Moon mg, the main constraints have been the range of mg among mare basalts and/or seismic velocity data. The resultant mg estimates (Table 6 includes a few examples) are often remarkably low compared to the absolute consensus (references cited above) for $89 \pm 1 \text{ mol}\%$ in the Earth's primitive mantle.

Buck and Toksöz (1980) and Mueller et al. (1988), among others, have used seismic velocity measurements to infer mg ~79 mol% for the Moon's upper mantle. However, as Cleary (1982) warned, only to be virtually ignored, these authors made unrealistic assumptions about the uncertainty in the lunar seismic profile. Improved results from the inverse Monte Carlo technique (Khan et al. 2000) show that mg is only loosely constrained by the seismic data, although the best estimates of Khan et al. (2000) suggest that seismic velocities are practically constant in the upper mantle down to ~500 km (amounting to 56% of the Moon). Figure 8 shows seismic velocities in this zone modeled based on the mineralspecific velocity compilation of Hood and Jones (1987), assuming 5% modal plagioclase, with the remainder being olivine + pyroxene in proportions ranging from 70:30 to 40: 60. The velocity estimates of Khan et al. (2000) are consistent with an mg of roughly 80 mol% for the upper mantle. But P waves suggest much higher mg (roughly 93 mol%!) than do S waves, and the ranges shown in Fig. 8 are far less than the full range of potentially valid seismic velocities found by Khan et al. (2000). Realistically, the uncertainties allow for mg anywhere from 50 mol% to well over 90 mol%. The deeper mantle has higher seismic velocities (Khan et al. 2000; Khan and Mosegaard 2001) that, in principle, suggest higher mg. However, increased uncertainties, plus the possibility of modal garnet (with P velocity ~20% higher than plagioclase) (Hood and Jones 1987), render interpretation in terms of lower mantle mg even more problematic than in the case of the upper mantle.

Oxide mg from Mare Samples

The notion that mare basalts can supply more than marginal constraints on bulk lunar mantle mg is likewise a facile approach based on a doubtful premise. Mare basalts are remarkably ferroan by terrestrial standards, with mg typically between 32 and 54 mol%; mare pyroclastic glasses have more moderate mg, typically 50-62 mol% (Taylor et al. 1991). Modeling these mg ratios as outcomes of simple equilibrium partial melting (assuming a K_D(Fe/Mg-crystals/melt of ~0.30) (Warren 1986) would suggest that the sources of typical crystalline basalts had mg = 61-80 mol% and that typical pyroclastic sources had mg = 77-84 mol%. The highest mg mare pyroclastic (66 mol% in Apollo 15 green glass "c"; Taylor et al. 1991) would have a source mg of 87 mol%. But in terms of Al₂O₃ versus mg systematics, even the green "c" composition (7.74 wt% Al₂O₃) plots at about 10 mol% lower mg than a typical terrestrial trend (Warren et al. Forthcoming).

However, as mentioned above, mare basalt is a tiny fraction of the Moon's crust, and the fraction of the mantle that could have played any direct role in mare petrogenesis is commensurately tiny, on an order of 2%. If the Moon's mantle were as well-stirred by convection as the mantle of the Earth, the limited volume involved would not matter. But instead, the lunar mantle is by all indications an extremely heterogeneous material and the heterogeneity stems from its origin as a pile of mafic (magmasphere) cumulates (e.g., Taylor 1982; Warren 1990; Beard et al. 1998). Mafic igneous cumulates form in "layered intrusions" that are notoriously heterogeneous in mg. Within layered intrusions, higher mg tends strongly to be associated with materials that have crystallized and would remelt at a higher temperature. In the terrestrial mantle, partial melting occurs at locales determined by plate tectonic motions and is thus almost indiscriminate with respect to composition. In contrast, the lunar mantle has not been well stirred since its origin as a mass of sunken magmasphere cumulates. Gross heterogeneity of the lunar mantle is manifested by, inter alia, enormous scatter in TiO₂ among mare basalts and by enormous isotopic heterogeneities (e.g., Beard et al. 1998).

Melting in such a context is surely not indiscriminate with respect to composition. Regions relatively low in mg, which would in general also be relatively rich in the heat sources, Th, U, and K, must be favored locales for partial melting. Nor is it sufficient, as some authors (e.g., Ringwood 1989; Jones and Delano 1986) have assumed, to identify mare samples with unfractionated ratios among the plagiophile and

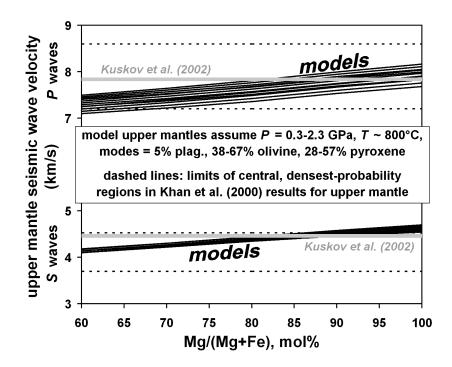


Fig. 8. The best estimates of Khan et al. (2000) indicate seismic velocities are practically constant in the upper lunar mantle; their results for P and S waves are shown here (dashed lines) as quasi-ranges. One caveat is that the ranges shown encompass only the central, densest-probability regions (corresponding to the two darkest colors in Fig. 1 of Khan et al. 2000) within much wider ranges spanned by the full Khan et al. (2000) dataset of potentially valid seismic velocities. Also shown are estimates for 60–500 km "consistent with mass and moment of inertia requirements" from Kuskov et al. (2002) (claimed uncertainties are about 5% relative). Shown for comparison as potential constraints on mg, are model seismic velocities based on the assumptions indicated and on mineral velocity data compiled by Hood and Jones (1987). In the models, the range of modal mineralogy is more important than the range in pressure; e.g., at the median upper mantle pressure (1.3 GPa) and an mg of 85 mol%, P velocity is much faster for olivine (8.02 km/s) than for low-Ca pyroxene (7.41) or plagioclase (6.6 km/s). For plagioclase, Hood and Jones (1987) did not list temperature and pressure derivatives; I have estimated them by analogy with averaged derivatives (normalized to STP velocities) for other minerals. The effect of temperature uncertainty is almost negligible, e.g., assuming 1050 °C would shift the model velocities down by 2% relative.

incompatible elements (Ca, Al, REE, Ti), e.g., the Apollo 15 green pyroclastic glasses. If the primordial magma ocean were a high degree melt of a Moon modestly endowed with plagioclase (Al₂O₃ and CaO; as inferred above), then a major degree of crystallization, implying mg fractionation, would have occurred before the onset of crystallization of any phase (plagioclase, ilmenite, etc.) capable of engendering noticeable fractionation among elements like Ca, Al, REE, and Ti. As noted by Arai and Warren (1999), mare pyroclastic glasses have on average about two times higher MgO/Al₂O₃ than crystalline mare basalts. Even allowing for the possibility that the data set may include a slight bias in favor of the low-MgO/ Al₂O₃ tops of the crystalline lava flows, this trend suggests that eruptions of volatile-rich magmas (i.e., products of relatively primitive, not completely volatile-depleted source regions) stem from source regions with far higher MgO (and mg) than the more processed regions that engendered the crystalline mare basalts. The only bottom line conclusion supported by the data for mg in mare samples is that the overall mantle mg is probably not far less than that implied by the most magnesian mare pyroclastic glass, i.e., 87 mol%.

Oxide mg from Highland Samples

In a companion paper, Warren et al. (Forthcoming) showed that the highland crust contains a component that is remarkably magnesian, considering that it is found in diluted form, within anorthositic, thoroughly polymict (mostly regolith) breccias. Extrapolation to the mg of an end-member magnesian component suggests a high, Earth-like oxide mg ratio for the Moon as a whole. Extrapolation direct to an Al₂O₃-poor mantle material, conceivably excavated by a giant basin-forming impact (e.g., to the Table 6 estimate for the bulk Moon: 3.8 wt%), would imply mg ~88-89 mol%. As discussed in the other paper (Warren et al. Forthcoming), a more likely scenario has the magnesian component representing the chemical signature of KREEP-poor varieties of Mg-suite cumulates formed within scattered intrusions of basaltic magma into the older, ferroan-anorthositic crust. If the magnesian component represents a good sampling of the crystallization products of a type of basaltic magma, with, say, 15-20 wt% Al₂O₃, then the extrapolated mg would be 80-84 mol% (Warren et al. Forthcoming). More generally, the material excavated and mixed into the surface regolith will

derive from fractionated subvolumes of the parent intrusions. However, the general tendency must be to preferentially excavate the upper portions of any given crustal intrusion, in which case the magnesian component suggested by the Al₂O₃-mg systematics (Warren et al. Forthcoming) would be ferroan compared to its parent melt. Unless the magnesian component is very strongly biased toward the deeper portions of its parent intrusion(s), it is unlikely to be much less magnesian than the primary mantle melt that was the antecedent of the intrusion(s). Such a deep-bias scenario cannot plausibly be invoked for more than a small, flukish subvolume of the lunar regolith. Yet the locus of the Al₂O₃mg trend (Warren et al. Forthcoming) would be much the same even without ALH 81005, as we now have Dhofar 025, another regolith breccia with mg greater than 70 mol%, which is obviously from a separate launch (Nishiizumi and Caffee 2001). Moreover, if the component represents primarily early, basal cumulates, then it ought to have a low Al₂O₃, because even assuming it formed after the onset of plagioclase saturation, the plagioclase would have tended to float. Thus the extrapolation from the Al₂O₃-mg trend (Warren et al. Forthcoming) should be to an Al₂O₃ of less than 15 wt%, implying an mg higher, and probably much higher, than 84 mol%. In other words, the Al₂O₃-mg trend confirms that the many pristine Mg-suite rocks with olivine mg upwards of 87 mol% (Warren 1993) are not flukish exceptions, but rather are representative of the early, near-liquidus olivines of magmas that constitute a major fraction of the lunar crust. Many individual Mg-suite troctolitic and ultramafic cumulates contain remarkably high-mg olivines, commonly Fo₈₉₋₉₀ and, in two instances, Fo₉₂ (Warren 1993). Also, as reviewed Ryder et al. (1997), Fo₈₇₋₉₄ olivines are a "prominent" component of Imbrium and Serenitatis impactmelt breccias. As Warren (1986) and Hess (1994) have discussed, special pleading is required to account for the petrogenesis of such olivines unless the bulk Moon mg is at least comparably high.

The average magma parental to this magnesian highland component is implied to be as magnesian, if not more magnesian, than most terrestrial magmas of comparable Al₂O₃ content. Consider first basalts, which have Al₂O₃ ~10-20 wt%. Of the many hundreds of samples of mid-ocean ridge basalt (MORB) that terrestrial petrologists have studied, the vast majority have mg between 50 and 66 mol%, the average being 61-62 mol%, and even "primary" MORB magmas are inferred to have had mg in the range 70-78 mol% (BVSP 1981). Ocean-island basalts, which are believed to arise from a distinct (deeper) mantle reservoir, generally have mg in the range 45-80 mol%, again the average being ~61 mol% (BVSP 1981). Data for komatiites from BVSP (1981) are shown in Warren et al. (Forthcoming). As reviewed by Arndt et al. (1997), in some individual locales the komatiites. komatiitic basalts and picrites plot a few mol% in mg above or below the trend of the BVSP (1981) data, but the trend shown is quite representative for terrestrial high-mg igneous rocks. The extrapolation of the KREEP-poor lunar highland trend (Warren et al. Forthcoming) passes far to the high-mg side of this terrestrial high-mg trend. Moreover, on a small, low-pressure body like the Moon, a magma that has liquidus olivine with mg in the range 87–90 mol% (as apparently was common for Mg-suite intrusions) (Warren 1993) can safely be assumed to have originally formed in a mantle with mg ~87–90 mol%.

This inference of a high mantle mg on the basis of Al₂O₃mg systematics (Warren et al. Forthcoming) can hardly be excused as an upper limit in the way that the mare-samples constraint is probably best viewed as only a lower limit for the bulk Moon mg. Large volumes of crust are probably involved, as the anticorrelation between mg and Al_2O_3 is manifested by a variety of lunaites (and KREEP-poor Apollo 14 and 16 regolith samples) from widely scattered regions. Although the era of Mg-suite magmatism was so early (Shih et al. 1993) that the lunar interior was probably highly convective compared to its increasingly moribund state during the mare-volcanism era, the circumstances of mantle melting were still probably not entirely controlled by tectonic motions. As with mare volcanism (see above), compositional selection, favoring low-melting, i.e., low-mg, portions of the mantle, may have already been a significant factor. Thus, the mg systematics of the KREEP-poor highland magnesian component may reflect a slight bias toward low mg.

To summarize, highland samples indicate that large portions of the lunar mantle that were prone to undergo melting during the Mg-suite era have mg \sim 87–90 mol%. By itself, this observation would suggest that the bulk mantle mg is at least 88 mol% and more likely 89 mol% or higher. Mare samples suggest that elsewhere, in small atypical portions of the mantle that managed to melt when lunar melt had become almost extinct, mg is diverse, ranging from ~87 down to ~60 mol%. On balance, the bulk mantle mg appears to be ~87–88 mol%. Assuming the crust contains roughly 25 wt% mafic silicates and thus contributes slightly less than 2% of the total lunar (MgO + FeO), and that the average mg of crustal mafic silicates is roughly 67 mol% (Warren et al. Forthcoming), the bulk Moon mg is lower than a bulk mantle mg estimate of 87-88 mol% by only 0.2 mol%. In other words, the estimated bulk Moon MgO/FeO ratio is ~3.9.

MgO and SiO₂

Having inferred Al_2O_3 and CaO concentrations and the MgO/FeO ratio, it only remains to infer the MgO/SiO₂ ratio to have all of the major oxides determined. Unfortunately, the bulk Moon MgO/SiO₂ ratio is not easily constrained. Even the limited pressure of the lunar interior has a strong tendency to stabilize pyroxene at the expense of olivine and thus could easily have engendered a pyroxene-dominated deep lunar mantle (Warren and Wasson 1979b), the common but naïve assumption that the earliest magma ocean cumulates (and/or

the deepest mantle restites) must be nearly pure olivine notwithstanding. Among chondrites (Wasson and Kallemeyn 1988; Jarosewich 1990), MgO/SiO₂ is fairly constant at 0.65 (±11%); the highest MgO/SiO₂ (0.70) is found in CI chondrites. Assuming MgO/FeO is roughly 3.9, the sum (MgO + SiO₂) must be slightly depleted relative to Al₂O₃, CaO, and other refractory lithophile elements. For example, if MgO/Th were chondritic, MgO would be ~39 wt% (see above), FeO ~10 wt% and (by difference) SiO₂ ~43 wt%. Such a model would imply a fractionation in the bulk Moon MgO/SiO₂ ratio to 1.30 times the CI-chondritic value and an implausibly low CIPW-normative pyroxene/(pyroxene + olivine) ratio of 0.18.

The volatility of MgO is not far less than that of SiO₂, so our provisional assumption of chondritic MgO/Th is subject to downward revision. Two lithophile elements only slightly more volatile than SiO₂ are Cr and Mn (Wasson 1985). As discussed in the next section, estimation of Cr is especially difficult and uncertain, but the Moon's MnO/MgO ratio is well constrained at a level (~0.24 times CI-chondritic) similar to that generally inferred for Earth's primitive mantle (Table 6; of course, highly volatile elements are obviously more depleted in the Moon than in the Earth). Absent better constraints, I extend this Earth-Moon analogy to infer that the bulk Moon MgO/SiO₂ is roughly 0.77. The resultant oxide concentrations are shown in Table 6.

To convey some sense of the uncertainty in these models, Table 6 includes several alternative models based on analogous methodology but with different assumptions regarding Th concentration and mg and MgO/SiO₂ ratios. The 0 °C, 0 bars (STP) density implied by a CIPW norm for the preferred composition (including an assumed 1.2 wt% of 8000 kg/m³ core) is ~3290 kg/m³, which agrees well with the bulk Moon value (3344 kg/m³; Konopliv et al. 1998) after translation to STP (e.g., Wood 2000). Given the various geophysical and density-modeling uncertainties, the density implied by the preferred bulk Moon composition allows for modest proportions of dense garnet and/or Mg-spinel in the deep mantle (and/or a slightly larger core).

Minor Trace Elements of Moderate Volatility and Vanadium

The most abundant of the lithophile elements remaining to be addressed are probably Cr and Mn; it is also convenient to simultaneously discuss V, another ferromagnesian transition element. These three elements have been the subject of a voluminous literature, attaching great significance to an inferred similarity between their depletion factors (in the bulk Moon versus chondrites) and the factors characteristic of the bulk Earth (e.g., Wänke and Dreibus 1986; Drake et al. 1989; Ringwood 1989; Ringwood et al. 1990, 1991). However, Ruzicka et al. (2001) noted that while Cr, Mn, and V do show a degree of similarity between the Moon and the Earth (for Cr and V this is hard to assess, because these elements are sensitive to spinel fractionation, which is sensitive to oxygen fugacity), the resemblance is equally impressive to the HED basalts of asteroidal provenance.

Even though Mn is only a minor element, it can estimated to virtually the same precision as the major constituent FeO. Among lunar samples FeO/MnO is remarkably constant at ~70 \pm 10 (e.g., Haskin and Warren 1991; Fig. 10 of Warren et al. Forthcoming). This method implies MnO = 0.13 wt%.

Assuming V is in chondritic proportion to Th and other refractory lithophile elements, the bulk Moon V would be ~133 µg/g. Rough V-Sc and V-Cr correlations (Fig. 9) suggest a depletion of V/Sc by a factor of three and a further depletion of Cr/V by a factor of two. A further clue is that, excluding high-Ti mare basalts, lunar rocks show a good Cr-Sc correlation, implying Cr/Sc depletion by a factor of five (Haskin and Warren 1991). Of these three elements, Cr is the most volatile, and it has been suggested (Ringwood et al. 1990; Gourant et al. 1992; Allègre et al. 1995; Wänke and Dreibus 1997; Gessman and Rubie 1998) that Cr, V, and Mn all may have become depleted by partitioning at extremely high pressure into the Earth's core. In contrast, Sc is a "regular" refractory lithophile element. However, all of these elements are partly compatible with major lunar minerals, especially pyroxene. If the available lunar samples are indirectly descended from a deep magma ocean that during most of its solidification crystallized roughly one-half pyroxene (mostly low-Ca) and one-half olivine (Warren and Wasson 1979b), then the composite D_{crystals/melt} would have been roughly 0.5 for Sc, 0.8 for V, and 2 for Cr (e.g., Kennedy et al. 1993; Ulmer 1989; Skulski et al. 1994; Hauri et al. 1994). If so, after, say, two-thirds fractional crystallization, forming "barren" ultramafic cumulates that would play little further active role in lunar magmatism (the bottom line effect of a smaller initial magma ocean plus a large proportion of "barren" restite would be similar), the residual magma ocean was enriched in Sc to 1.7 times the initial concentration and in V to 1.2 times, while being depleted in Cr to ~0.33 times the initial concentration. Thus, the observed Cr/Sc depletion does not imply major loss of Cr as a volatile. However, the observed V/Sc ratio seems too greatly depleted (by approximately one-third) to explain purely as result of olivine- and pyroxene-dominated igneous differentiation, and Cr seems clearly further depleted relative to V (Fig. 9). These admittedly somewhat inconsistent results suggest that bulk Moon V and Cr are depleted by factors of roughly 0.7 and 0.4, respectively, relative to refractory lithophile elements, implying concentrations of 100 and 3000 μ g/g, respectively.

These V and Cr estimates should be considered extremely uncertain, and are probably best viewed as upper limits. It is impossible to gauge to what extent Mg-rich spinel, which has a strong affinity for V and Cr (note the position of a rare Mg-spinel troctolite clast in Fig. 9), may have crystallized early from the lunar magma ocean or otherwise

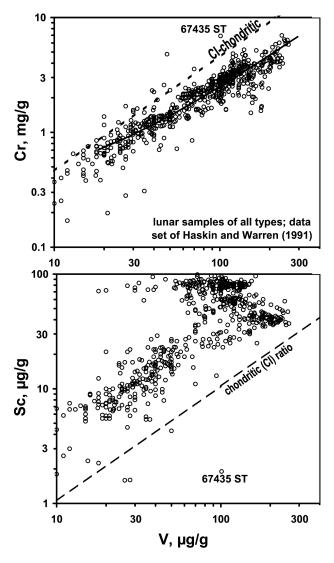


Fig. 9. V versus Cr and Sc for lunar samples, used to infer the bulk Moon Cr and V concentrations (see text). The data set of Haskin and Warren (1991) was used to construct this plot, except V data from the USGS (H. J. Rose) and Oslo (A. O. Brunfelt) labs have been discarded; by large factors, data from the former source appear systematically low, and from the latter, systematically high. Scatter at high end of the V-Sc correlation reflects enormous ilmenite fractionation effects among mare basalts. Note that spinel, as exemplified by the "pink spinel troctolite" clast from Apollo 16 breccia 67435 (Ma et al. 1981) (Cr = 5.1 mg/g, V = 101 µg/g), can potentially act as a sop for V and Cr.

during deep-seated early magmatism. Spinel stability is such a strong function of oxygen fugacity that it is extremely difficult to predict its relationship to the liquidus during fractional crystallization of even a known composition, and of course the detailed composition (and bottom pressure) of the magma ocean is unknown. The eucrite basalts of the HED asteroid feature the same factor of five depletion in Cr/Sc, and a factor of three to four depletion in V/Sc, as in lunar basalts. But V is refractory, and 80% loss of Cr as a volatile is implausible for the HED asteroid, because Mn, which is slightly more volatile, is so little depleted that even though the HED asteroid is probably more FeO-rich than the Moon (Dreibus et al. 1977; Hertogen et al. 1977) eucrites feature MnO/FeO fully two times the lunar ratio (Fig. 10 of Warren et al. Forthcoming).

A comprehensive assessment of the bulk Moon composition, including trace elements that are lithophile but much more volatile than the major elements (and therefore must each be evaluated individually), and siderophile elements whose concentrations were determined by metalsilicate fractionation (which again, generally requires individual evaluation), is beyond the scope of this paper. Most such elements are only indirectly constrained by lunaites and orbital GRS data.

For completeness in terms of the commonly discussed oxides, we will briefly address Na and K. The easiest of these is K, which shows an excellent correlation with Th (Fig. 5), implying a bulk Moon K/Th ratio of ~600, and thus ~42 μ g/g K. As with the mg ratio, the common approach in past estimates of the bulk Moon Na content has been to emphasize the superficially familiar (Earth-like) rock type of mare basalt. However, a significantly different perspective is gained from consideration of highland samples. The volumetrically dominant ferroan anorthosite component of the nonmare crust is largely defined (e.g., Warren 1990) on the basis of plagioclase Na/Ca ratio, which is only about half the typical value than in otherwise comparable lunar rock types. Relying mainly upon a very loose correlation between Na and K, and giving comparable weight to highland and mare trends, we can infer a bulk Moon value of roughly 0.05 wt% for Na₂O. Finally, this estimate for Na can easily be translated into one for Ga, based on the correlation between Ga and Na among lunar samples in particular and planetary materials in general (implicit in Fig. 10 of Warren et al. Forthcoming). The resultant estimate for bulk Moon Ga is ~ $0.5 \,\mu g/g$.

Comparison with Earth's Primitive Mantle

The inferred bulk composition of the Moon is compared with the consensus estimate for Earth's primitive mantle in Table 6 and Fig. 10. To reiterate, the results for V and Cr are dubious, as no allowance has been made for the wild card possibility of deep-interior Mg-spinel fractionation. Thus, the striking similarity of the dips at V is potentially misleading. Essentially the same V-Cr relationships hold for basaltic materials from the HED asteroid (cf. Ruzicka et al. 2001), a body that no one has ever suggested shares a special genetic link with Earth. Münker et al. (2003) find that the ratio Nb/Ta is almost precisely chondritic in the Moon, despite evidence (e.g., Wade and Wood 2001) that at high pressures in the deep Earth Nb, like Cr, V, and Mn, becomes weakly siderophile and, if so, may have partly sequestered into the core.

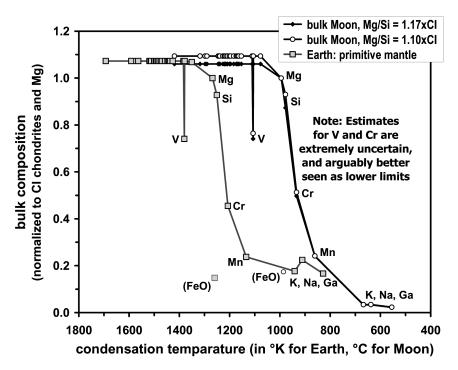


Fig. 10. The bulk composition of the Moon and the consensus estimate for Earth's primitive mantle, normalized to Mg and CI chondrites, plotted against Wasson's (1985) calculated temperatures for 50% condensation of the elements from a solar nebula gas at 10^{-5} atm. The estimates for V and Cr may be too low if major proportions of spinel are sequestered in the deep mantle (see text).

Nonetheless, the Earth-Moon similarity in terms of MnO and FeO is impressive (Fig. 11). Mn is significantly more volatile than the major elements and FeO (i.e., the degree of oxidation of total Fe) is tremendously diverse among primitive meteorites. The similarity in terms of refractory lithophile elements would be unsurprising (no other solar system body has ever been shown to be much different in this respect) were there not voluminous literature (e.g., Morgan et al. 1978; Taylor 1982; Drake 1986; Newsom and Taylor 1989; Taylor 1999) suggesting that these elements are substantially enriched in the Moon versus the Earth's primitive mantle and chondritic materials, and with some models (e.g., Cameron and Ward 1976) predicting such an enrichment as a byproduct of lunar origin by giant impact.

If anything, vis-à-vis the canonical giant impact model of lunar origin, the compositional similarity between the Moon and Earth's primitive mantle is too close. Isotopic results for oxygen (Clayton and Mayeda 1996) and Cr (Lugmair and Shukolyukov 1998; Birck et al. 1999), among other parameters (Fig. 11), show that the only real "Mars-sized body" for which we have data is compositionally distinct from Earth and its Moon. Detailed modeling of the impact consistently suggests that at least 75% of the lunar material comes from the late-arriving, and in a sense interloping, giant impactor (Canup 2004; cf. Benz et al. 1986; Melosh and Sonnett 1986; Canup and Asphaug 2001). Even assuming the giant interloper/impactor was compositionally identical to the rest of the final Earth, the giant impact process must (to account for the Moon's grossly depleted Fe-metal content) have entailed compositional differentiation.

It is not obvious that this differentiation would stop at metal-silicate separation. The protolunar matter would probably have to pass through a volatilization/condensation cycle (e.g., Ida et al. 1997; Stewart 2000), which might engender refractory enrichments in the final Moon (as originally suggested by Cameron and Ward 1976) or fractionation of FeO (and thus MgO/FeO), MnO, and other moderately volatile species. FeO is considerably more volatile than MgO and even SiO₂ (e.g., Grossman and Larimer 1974; Hashimoto 1983; Petaev and Wood 1998). Experiments by Wang et al. (2001; cf. Cohen et al. 2004) indicate that during evaporation of CI chondritic matter, before the refractory lithophiles (Al₂O₃, CaO, Th, etc.) are enriched to any detectable extent, say, 10%, versus the moderately volatile major elements (SiO₂ + MgO), so much FeO is lost that the ratio $FeO/(SiO_2 + MgO)$ is reduced to less than half of the starting ratio (Fig. 12). An enrichment factor of 1.6 for refractory lithophiles versus SiO₂ + MgO as advocated by Taylor (1982, 1999) would imply near-total loss of FeO. Taylor (1987) acknowledged that enrichment of refractory elements through a volatilization/condensation cycle would be unlikely without concomitant depletion of FeO and speculated that the orbiting debris cloud that formed the Moon (derived preponderantly from the giant impactor) had an FeO concentration of ~36 wt%, i.e., nearly five times that of Earth's primitive mantle (Table 6). Newsom and

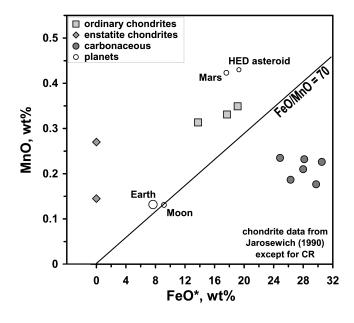


Fig. 11. Plot of FeO versus MnO for chondritic meteorite types (Jarosewich, 1990) and estimated bulk planetary compositions. The x-axis is labeled FeO* because for some types of chondrites, data for Fe₂O₃ have been translated (multiplied times 0.90) into FeO. The bulk planetary compositions are from (for Earth and the Moon) Table 6; also (for Mars) average of Longhi et al. (1992), Lodders and Fegley (1997) and Sanloup et al. (1999), and (for the HED asteroid) average of Hertogen et al. (1977) and Dreibus et al. (1977).

Taylor (1989) suggested instead that enrichments in both refractory lithophiles and FeO were simply inherited (without post-impact volatilization/condensation effects) from the bulk impactor composition. But this only pushes the problem of the mechanism for refractory enrichment (and yet little or no FeO loss) back without solving it. If the Moon's matter came so preponderantly from such an unEarth-like body, the close match between the Moon and Earth for such incontrovertible parameters as oxygen and Cr isotopes and FeO/MnO ratio (Fig. 11) would all seem remarkably fortuitous.

As Warren (1992) pointed out, lithophile element fractionations, and in particular refractory-lithophile enrichments, might also arise independently of vaporizationcondensation processing. The orbiting impact debris that eventually forms the Moon is metal-depleted (a crucial advantage of the model) because it is preferentially derived from the peripheral portions of the two impacted bodies (particularly if jetting [Melosh and Sonnett 1986] plays a major role). But assuming one (or both) of the impacting bodies had differentiated into a crust-over-mantle structure, or even just a large proportion of mantle cumulates surmounted by molten magma ocean, this shallow-provenance bias would inevitably also imply a fractionated bulk Moon oxide composition. One of the most inevitable fractionations under such a scenario would be an enrichment of refractory lithophiles, because Al2O3, CaO, Th, etc. would have concentrated into any crust that was extant. However, there

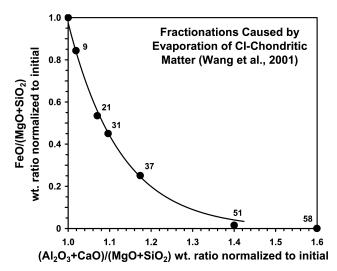


Fig. 12. Fractionations of key ratios (i.e., ratios that according to some models are highly fractionated in the bulk Moon versus Earth's primitive mantle) engendered during evaporation of CI-chondritic matter. This plot is based entirely on experimental results summarized in Fig. 8 of Wang et al. (2001), but Cohen et al. (2004) have reported very similar results. Numbers along curve indicate percent of total mass loss in the experiments.

would also be fractionations among the refractory lithophile elements. For example, light REE should be enriched over heavy REE (Warren 1992). If anything, Nd isotopic data for ferroan anorthosites point toward a light REE depletion in the bulk Moon (Borg et al. 1999). The strong compositional similarity between the Moon and Earth's primitive mantle requires not only that the giant impactor derived from the same well-mixed portion of the solar system as the main mass of the Earth, but also that both bodies were fully molten, or at least nearly so (and thus undifferentiated, except for coremantle separation), before the impact.

Among alternatives to the giant impact, the venerable hypothesis of intact capture is obviously ill-suited to explain extreme compositional kinship between the Moon and Earth. Wasson and Warren's (1979) modified coaccretion model, in which a multitude of smaller collisions accomplished metalsilicate separation long before the protolunar material came into proximity with Earth, is difficult to quantitatively test with available physical modeling tools, but admittedly coaccretion appears ill-suited to match the very high angular momentum of the Earth-Moon system (Herbert et al. 1986; Weidenschilling et al. 1986).

CONCLUSIONS

Based on comparisons with sample ground truth, the recent recalibration for Lunar Prospector global Th data (Prettyman et al. 2002; Lawrence et al. 2003) is a major improvement. However, the calibration still yields implausibly high concentration results for the three most Thpoor documented sampling sites, especially Luna 24, it still extrapolates to a nonzero LP-GRS Th, ~0.7 μ g/g, at zero sample Th, and it still results in a misfit toward too-high Th when compared with the global regolith Th spectrum as constrained using mainly lunaite regolith breccias. It appears that areas with true Th concentrations of less than about 0.5 μ g/g, which lunaites suggest comprise nearly half of the lunar surface, are yielding LP-GRS results that are too high by a large factor, typically approximately 1.5.

Another problem is manifested by a Th versus K diagram including Lunar Prospector data for K (Prettyman et al. 2002). Ground truth data plot consistently to the high-Th/K side of the Prospector data trend, offset by a factor of 1.2. This is probably a separate and distinct problem, because it extends equally to Th-rich samples. It is difficult to determine whether this offset stems mainly from a faulty calibration for Th, for K, or for both.

In view of the history of major calibration revisions for Th (Lawrence et al. 1999, 2000; Prettyman et al. 2002) and the apparent need for yet further revision, it seems increasingly clear that an empirical approach, based largely on ground truth, may ultimately be the best method for calibration of the LP-GRS Th data. A new calibration is proposed that represents a compromise between the Th levels indicated by ground truth constraints and the Prettyman et al. (2002) calibration. Conservatively assuming that the Th versus K issue is mostly a K problem, the average global surface Th is estimated to be ~1.35 µg/g, in agreement with an estimate of 1.3 µg/g derived by Metzger et al. (1977) from extrapolation of Apollo GRS Th data for ~20% of the surface.

The Moon's remarkable global asymmetry in KREEP abundance is even more pronounced than previously supposed. The surface Th concentration ratio between the hemisphere antipodal to the Procellarum basin and the hemisphere centered on Procellarum has been reduced from 0.48 in the Lawrence et al. (2000) calibration to 0.24 in the new one. This extreme disparity is most simply interpreted as a consequence of origin of Procellarum at a time when the Moon still contained at least a thin residual layer of global magma ocean.

Assuming a crustal thickness of 48 km and allowing for diminution of Th with depth (Warren 2001b), the extrapolated bulk crustal Th is ~0.73 μ g/g. Further extrapolation to bulk Moon Th yields ~0.07 μ g/g, which is nearly identical to the consensus estimate for Th in Earth's primitive mantle. Assuming chondritic proportionality among refractory lithophile elements, the bulk Moon concentrations of Al₂O₃ and CaO are ~3.8 and 3.0 wt%, respectively.

The Moon's bulk mantle mg ratio is only weakly constrained by seismic data and mare-basaltic data. A strong anticorrelation between mg and Al_2O_3 among KREEP-free highland polymict (especially regolith) samples, many of them lunaites, suggests for the bulk Moon a very Earth-like oxide mg ratio of ~87–88 mol%. The close resemblance between the bulk Moon and Earth's primitive mantle extends

to moderately volatile elements, most notably Mn. Earth-like concentrations are also inferred for bulk Moon Cr and V (a refractory element), but for these particular elements the inferences are extremely uncertain because major proportions of Cr and V are possibly sequestered into mantle spinel.

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