

## The origin of the Moon and the early history of the Earth—A chemical model. Part 1: The Moon

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(Received February 28, 1990; accepted in revised form January 17, 1991)

**Abstract**—The chemical implications of a “giant impact” model for the origin of the Moon are examined, both for the Moon and for the Earth. The Impactor is taken to be an approximately Mars-sized body. It is argued that the likeliest bulk chemical composition of the Moon (including a small Ni-rich metallic core) is quite similar to that of the Earth's mantle, and that this composition may be explained in detail if about 80% of the Moon came from the primitive Earth's mantle after segregation of the Earth's core. The other 20% of the Moon is modelled as coming from (a) the Impactor, which is constrained to be an oxidized, probably undifferentiated body of roughly CI chondritic composition (on a volatile free basis) and (b) a late stage veneer, with a composition and oxidation state similar to that of the H-group ordinary chondrites. This latter component is the source of all the volatile elements in the Moon (e.g., Na, K, Rb, Cs, and the volatile siderophile elements such as Cu, Ge, etc.), which failed to condense from the Earth- and Impactor-derived materials; this component constitutes about 4% of the Moon. It is argued that Mo may behave as a volatile element under the relatively oxidising conditions necessary for the condensation of the proto-Moon.

The late stage veneer may also be the reducing agent responsible for forming a small lunar core, which depletes the primitive silicate mantle of the Moon in the more siderophile elements. This core is presumed to have formed in equilibrium with the lunar mantle and, therefore, has  $\text{Ni}/(\text{Ni} + \text{Fe}) = 0.45 \pm 0.1$ ; a mass balance of Ni in the Moon constrains the lunar core to  $\sim 1\%$  of the Moon's mass. Metal separation to the core at an assumed temperature of  $1300^\circ\text{C}$  takes place at an oxygen fugacity 0.8 log-bar units below the iron-wüstite (IW) oxygen buffer. These conditions may then be used to calculate the siderophile trace element concentrations in the core-forming metal and thus the siderophile element abundances of the bulk Moon (core plus primitive mantle). The model accounts satisfactorily for most of the siderophile elements, including Fe, Ni, Co, W, P, and Cu. The relatively well-constrained lunar abundances of V, Cr, and Mn are also accounted for; their depletion in the Moon is inherited from the Earth's mantle. The consequences of the model for the composition of the Earth's mantle are addressed in O'Neill (1991).

### INTRODUCTION

SERIOUS SCIENTIFIC speculation on the origin of the Moon seems to have begun with the hypothesis of Darwin (1879, 1880) that the Moon formed by fission from the Earth. Since then, the twin questions of whether the chemistry of the Moon is similar to that of the Earth and, if so, whether this implies a genetic relationship have been the chief aspects of the topic of concern to geochemists (e.g., RINGWOOD, 1966). Interest in the matter naturally began to increase rapidly with the Apollo and Luna missions, although the availability of returned samples and the mass of data gathered did not lead to any notable degree of agreement; contrast, for example, the almost opposing conclusions on lunar origins reached in the monographs of RINGWOOD (1979) and TAYLOR (1982).

Recently, a new consensus has begun to emerge that the Moon originated following the collision of a third planetary body, Mars-sized or larger, with the early Earth. Such a huge impact is thought to have resulted in a large amount of material being thrown into Earth orbit, some of which re-accreted to form the Moon. Although this type of “giant impact” model satisfies most of the dynamic and other physical constraints on lunar origin, which competing theories such as fission, capture, or binary accretion have failed to do (WOOD, 1986; STEVENSON, 1987; NEWSOM and TAYLOR, 1989), it

has so far largely left unanswered the major geochemical questions; this has not, however, been for lack of attempts. For some, the giant Impactor has “cut the Gordian Knot” of the lunar origins problem by providing a planet-like source for the Moon, which is not the Earth (TAYLOR, 1986a,b, 1987; NEWSOM and TAYLOR, 1989). For others, the Impactor simply provides a means of ejecting material from the Earth's mantle (WÄNKE and DREIBUS, 1986). A related view accepts that the Impactor may be responsible for the high angular momentum of the Earth–Moon system, but argues that the Moon was then derived from the Earth's mantle by other means after this event (RINGWOOD, 1989a,b). Thus, the basic geochemical questions remain the subject of contention. It must be admitted that the recent dynamical modelling of the collision process seems to favour deriving the lunar material from the Impactor (e.g., BENZ et al., 1989), but to some extent the input to such models has already been influenced by the presumed geochemical outcome—the assumption, for example, that the Impactor is a differentiated planet with a dense metallic core. Furthermore, such scenarios tend merely to put back a step, to the Impactor, the question of how the material making up the Moon acquired its rather peculiar chemistry.

The problem of the chemical connection between the Earth and the Moon may be summed up as follows (see also Drake,

1986): both the Earth's upper mantle and the Moon share identical oxygen isotope patterns, indicating an origin in at least the same part of the solar system. Both are usually considered to have chondritic (solar) relative abundances of the refractory lithophile elements (Ca, Al, Ti, REE, etc.). The volatile elements are clearly depleted in the Moon relative to the Earth (itself depleted in volatiles compared to chondritic), but this is to be expected in most models whether or not the lunar material originated from the Earth. There remains a lively controversy as to whether the Moon is also more enriched than the Earth in its absolute abundances of the refractory elements (i.e., relative to Si and perhaps Mg); this subject will be briefly reviewed below. The siderophile element inventory of the Moon (silicate portion) shows a rather idiosyncratic pattern of depletion, similar to, but definitely not identical with, that of the Earth's mantle. The Moon appears more depleted than the Earth in many of the more highly siderophile elements, such as Ni (by a factor of 3 to 5), but actually a little less depleted in a few of the less siderophile elements, most noticeably Fe. However, as argued by RINGWOOD (1979, 1986a,b), the siderophile patterns in the Earth and Moon are really rather similar, and neither can be explained by an straightforward metal fractionation process starting from initially chondritic material, at least under conditions of chemical equilibrium at the low to moderate pressures presently accessible to experimental investigation. This state of affairs contrasts with what seems to be a relatively straightforward signature of metal fractionation in the Eucrite Parent Body (DREIBUS and WÄNKE, 1980), and of metal/sulfide fractionation in the SNC Parent Body (which is probably Mars), as discussed by TREIMAN et al. (1986) and WÄNKE and DREIBUS (1988). Indeed, the anomalous overabundance of many of the moderately siderophile elements in the Earth's mantle (most conspicuously Ni) and the related conundrum of why the mantle is so oxidized (O'NEILL and WALL, 1987) are amongst the most important unsolved mysteries in the geological sciences.

The recognition that the Moon itself probably has a small metallic core (limited to less than about 2% of its mass) meant that the total abundances of the highly siderophile elements in the Moon might be revised upwards, improving the match with the Earth's upper mantle. A thermochemically based discussion of silicate-metal equilibria and core formation in the Moon has been given by SEIFERT et al. (1988) for the major elements Fe and Ni. Taking the Fe/Ni ratio of the lunar mantle as the starting point and assuming thermodynamic equilibrium at appropriate temperatures and pressures, one may calculate not only the Fe/Ni ratio of any metal which precipitated from the lunar mantle to form the lunar core, but also the oxygen fugacity at which this occurred. This then allows the abundances in the lunar core of a number of other siderophile elements to be calculated, using experimentally determined metal/silicate distribution coefficients. Hence, the siderophile content of the bulk Moon may be estimated for any assumed size of lunar core. The result shows that the Moon must be formed from silicate material already rather uniformly depleted in a range of elements with different siderophile tendencies, including both Fe and Ni. The only other such material in the solar system found so far is that which makes up the Earth's mantle.

Clearly, then, there is *prima facie* evidence of a close relationship between the Earth and the Moon. An assessment as to whether this similarity implies a genetic connection or whether it merely reflects similar processes operating independently in two different planetary bodies (NEWSOM and TAYLOR, 1989) can only be made if we know what these processes are. Thus, models for the origin of the Moon are inescapably bound up with explanations for the siderophile element anomaly in the Earth's mantle.

The aim of this paper is to use the basic idea that the Moon was formed as a result of a giant impact, as the starting point from which to develop a model to account for the chemical compositions of both the Moon and the Earth. That there are differences in the compositions of the two bodies (e.g., FeO content) argues against a straightforward fission hypothesis. The early giant impact models (HARTMANN and DAVIS, 1975; CAMERON and WARD, 1976) suggested that a mixture of material from both the Earth's mantle and the Impactor would be ejected into Earth's orbit, eventually forming the Moon. This kind of model has the attractive feature from the chemical point of view that it allows for the possibility of the Moon being derived mostly from the Earth, thus explaining the similarities, but with sufficient extra material to account also for the differences. Moreover, the addition of something like 10–15% extra chondritic material to the Earth (which is the presumed size of the Impactor on dynamical grounds) would be capable of radically altering the trace and minor element chemistry of the mantle, thus suggesting a means of accounting for the siderophile element anomaly. It may be noted that the mantle abundances of Ni and many of the other moderately siderophile elements do indeed fall in the range 10–15%, chondrite normalized. However, a simple mass balance of the type "proto-Earth + Impactor = Earth + Moon" can be shown to be too naive a story; one must also take into account further modification of the chemical composition of both planetary mantles by such processes as volatilization, core formation, and additional accretion of late stage material. The model presented here will make provision for these complications. In doing so it will be necessary to assess the evidence on the composition of both planetary bodies and the way they may be modified by such chemical processes. This will then allow the model to be tested quantitatively against the evidence. Because of the complexity of the problem, it is convenient to proceed by first outlining the model. The bulk composition of the silicate portion of the Moon will then be assessed and will be used to calculate the composition of a lunar core. Finally, for the siderophile elements, the integrated lunar composition (silicate portion plus core) will be compared to the predicted model composition. The further implications of the model for the siderophile element abundances in the Earth's mantle and the early history of the Earth will be addressed in a companion paper (O'Neill, 1991)

#### OUTLINE OF THE MODEL

Both the Moon and the Earth are presumed to be made up of three components, namely, (a) that constituting the Earth before the impact (the "proto-Earth"); (b) the Impactor; and (c) a late stage veneer. The sequence of events is taken to be as follows:

- 1) The proto-Earth has a mass of about 90% of the present Earth. Its oxidation state is very reduced, with most of the Fe and all of the moderately to highly siderophile elements (Ni, Co, W, Pt-group) in the core. The Mg# of the mantle is 0.97. The slightly siderophile elements V and Cr are substantially partitioned into the core, as is a little Si. The proto-Earth is also depleted in the volatile elements. It is probably still hot from the energy released by accretion and core formation.

The "Mars-sized Impactor" is an oxidized body of roughly chondritic composition (assume CI for refractory and moderately volatile elements), with a mass 11% of the present Earth, on a volatile-free basis.

- 2) Collision of the Impactor with the proto-Earth releases enormous energy and throws material from the Impactor and a substantial fraction of the proto-Earth's mantle into orbit. Geochemically, it is the proportion of Impactor to proto-Earth thrown into orbit and volatilised which matters. For convenience I assume that all the Impactor and 50% of the proto-Earth's mantle is volatilised, but identical results follow if, say,  $\frac{1}{4}$  of the Impactor and  $\frac{1}{8}$  of the proto-Earth's mantle are taken instead. Similarly, I assume that no refractory material is lost from the Earth-Moon system. Material which has not been volatilised returns to the Earth, together with some recondensed material. A percent or so of the volatilised material remains in orbit; this will form the proto-Moon.
- 3) The Earth is now 99% of its present mass. The mixing of the Impactor material (oxidised) with the original proto-Earth's mantle (reduced) results in a net oxidation state close to that presently observed, near the QFM (Quartz-Fayalite-Magnetite) oxygen buffer (O'NEILL and WALL, 1987). Precipitation of a small amount (0.2 wt% of the mantle) of a Fe-Ni-S-O liquid (named here the "Hadean matte") moves to the core, the amount being controlled by the availability of S. The present abundances of the moderately siderophile elements (Fe, Ni, Co, W, etc.) are established, but the mantle is completely depleted in the highly siderophile elements (e.g., Pt group) and S.
- 4) Meanwhile, the material still in the Earth's orbit condenses to form the proto-Moon, which is hot (magma ocean?) and has an oxidation state above the level required for metal precipitation. Elements more volatile than Li or Mn fail to condense and are quantitatively lost, so that the proto-Moon is volatile free. In contrast to the Earth at this stage, there is no precipitation of matte or metal to form a core, because no S (a volatile element) has condensed.
- 5) Late-stage bombardment of both the Earth and the proto-Moon by reduced chondritic material with an average composition something like the H-group ordinary chondrites follows. The amount accreted to the Earth is approximately 0.5–1% of the mass of the mantle; this is the late stage veneer, which establishes the abundances of the highly siderophile elements in the Earth's mantle.

The Moon has 1.8% of the mass of the Earth's mantle, but a cross-sectional area 7.5% of the Earth's; hence, a 1% late veneer to the Earth's mantle should result in a 4% addition to the Moon (a more sophisticated analysis of this problem

has been given by SINGER and BANDERMANN, 1970, and BANDERMANN and SINGER, 1973; their equations reduce to this simple proportionality when the mean geocentric velocity of the accreting bodies becomes large relative to the escape velocity of the Earth, as is the case for modern meteorite impacts). This component is required to supply all the Moon's complement of the volatile elements. The addition of this metal-containing reducing material to the proto-Moon also results in the precipitation of a small Ni-rich lunar core, with a mass of 1% of the Moon.

In this model the composition of the Moon is subtly but identifiably different from that of the Earth's mantle because (a) the ratio of Impactor to proto-Earth material is higher in the Moon, (b) volatiles from the proto-Earth and the Impactor do not condense to the Moon, and (c) the Moon receives about 4 times the late stage veneer.

### Constraints on the Various Components

In order to minimize the number of variables in the model, I proceed under the restriction that both the Impactor and the material of the late stage veneer will have readily observable compositional analogues in the present solar system. The philosophical advantage of this assumption is that, although it may leave open the question of how these particular compositions were themselves formed from the solar nebula, it does at least guarantee that such compositions are possible, perhaps even likely, materials for planet building in this solar system. The model then effectively contains eight variables, the details of which need to be further specified:

- 1) Mass of the Impactor,
- 2) Composition and oxidation state of the Impactor,
- 3) Ratio of the mass of the Impactor to the fraction of the proto-Earth's mantle which is vaporised,
- 4) Composition and oxidation state of the late veneer,
- 5) Amount of the late veneer in the Earth,
- 6) Amount of the late veneer in the Moon,
- 7) Size of the lunar core, and
- 8) Amount of the "Hadean matte" lost to the core in the Earth.

The dynamical constraints favour the mass of the giant Impactor to be about 10–15% of the present Earth (e.g., BENZ et al., 1989). A mass balance of the siderophile element Ni suggests that 11% (i.e., 16% of the present mantle + crust) is appropriate, if it is assumed that all the Ni now in the mantle came from the Impactor plus the late veneer, and allowing for a little Ni lost in the "Hadean matte" to the core, and some to the Moon. The composition of this material is required to be chondritic for the refractory and moderately volatile siderophile elements, and nearly so for the very volatile (e.g., Zn, In), although this is poorly constrained. It must also be oxidised (all Fe as FeO or some Fe<sub>2</sub>O<sub>3</sub>). CI material is assumed.

For the Moon, the ratio of Impactor (plus late veneer) to material from the proto-Earth's mantle was adjusted to give a suitable lunar Mg# (0.83).

The late veneer provides the Moon with its complement of the volatile elements and may also be the reducing agent which forms the lunar core. The composition and oxidation

state of type 3 H-group ordinary chondrites (as given in Table 2 of WASSON and KALLEMYN, 1988) is suitable, although a more metamorphosed type would provide a better match for the lunar abundances of the highly volatile elements. The abundances of the moderately volatile lithophile elements suggest that the addition of 4% of this material is necessary.

The late veneer in the Earth's mantle requires only 0.5–1% of similar material.

The size of the lunar core is estimated from a mass balance of Ni in the Moon. This particular variable is something that one might hope will eventually be determined by geophysical measurements.

The amount of the Hadean matte lost to the Earth's core after the impact is constrained to be (a) small enough so as not to perturb the Ni/Co ratio of the Earth to more than 10% below chondritic, and (b) large enough to deplete the highly siderophile elements (i.e., those with silicate/matte partition coefficients  $>10^4$ ) to less than 0.1% of chondritic. 0.2% of the mantle seems approximately appropriate.

The bulk composition of the Earth's upper mantle plus crust (hereafter referred to as the "Earth's mantle") is largely taken from WÄNKE et al. (1984) and is given in Table 1. The WÄNKE et al. (1984) estimate is mostly based on analyses of ultramafic xenoliths deemed to be "primitive," following the work of JAGOUTZ et al. (1979); see also HART and ZINDLER (1986). The abundances of a couple of interesting elements

not covered by WÄNKE et al. (1984), Mo and Sn, were estimated from other sources, and the abundances of a few more have been altered to take into account new data (see Table 1 for details). For most elements these abundances are also very similar to the estimates of SUN (1982) and ANDERSON (1983), obtained using rather different methods and assumptions. The abundance of the important element S in the mantle is discussed in more detail in O'NEILL (1991, Appendix 1).

The details of the mass balance between the proto-Earth's mantle, the Impactor, and the late veneer are arranged as follows. Let the mass of the present Earth be  $M_E$ . The mass of the present Earth's mantle is  $0.68M_E$ , and of the Moon is  $0.012M_E$ , giving a net mass for the Earth's mantle plus Moon system of  $0.692M_E$ . The mass of the Impactor is taken as  $0.11M_E$ , and the total amount of late-stage veneer is  $0.004M_E$ . The mass of the proto-Earth's mantle is then  $0.578M_E$ .

The proportion of Impactor in the mix which forms the Moon is  $0.11/(0.578*f + 0.11)$ , where  $f$  is the fraction of the proto-Earth's mantle vaporised along with the Impactor. For  $f = 0.5$  (a conveniently round figure, but actually chosen to produce a suitable lunar Mg#), this proportion is 27.6%. The proportion of Impactor in the present Earth's mantle is  $(0.11 - 0.276*0.012)/0.68$ , or  $\sim 16\%$ .

Let the composition of the Impactor be **I** and that of the proto-Earth's mantle be **pE**. The composition of the Moon is thus

$$\mathbf{M} = (0.11 \mathbf{I} + 0.578 f \mathbf{pE}) / (0.11 + 0.578 f) \quad (1)$$

where the denominator renormalises to 100%. The composition of the present Earth's mantle (neglecting for the moment the addition of the late-stage veneer and the removal of the Hadean matte) is

$$\mathbf{E} = [(0.11 - 0.276*0.012) / (0.578 - 0.724*0.012)] \mathbf{pE} / 0.678. \quad (2)$$

Rearranging to eliminate **pE** produces, for  $f = 0.5$ ,

$$\mathbf{M} = 0.14 \mathbf{I} + 0.86 \mathbf{E}. \quad (3)$$

In other words, the refractory element composition of the bulk Moon before the late-stage veneer should appear to be composed of 14% Impactor and 86% present Earth's mantle.

Adding in the 4% late-stage material and taking into account the loss from the present Earth's mantle of the Hadean matte, and again renormalising to 100%, gives the following presumed bulk composition of the Moon for refractory elements:

- 82.5% of the present Earth's mantle
- 0.2% Hadean matte
- 13.3% (volatile free) CI material
- 4% H chondrite material.

Because the composition of the Hadean matte is poorly known, the model lunar abundances of the siderophile refractory elements (assumed to be completely removed from the proto-Earth's mantle) are better computed from

- 26.5% of (volatile free) CI material (i.e.,  $27.6%*0.96$ )
- 4% H chondrite material.

This model lunar composition is given in Table 1. Note that the oxygen making up the Moon is mostly derived from

Table 1. Model composition of the primitive bulk Moon. Volatiles (marked \*) are supplied only from the "H-chondrite" contribution. Siderophiles (in parentheses) are further depleted by core formation.

Element	Earth's Upper Mantle <sup>a</sup>	CI (volatile free) <sup>b,f</sup>	H-group chondrites <sup>b</sup>	Primitive Bulk Moon
Mg %	22.2	14.2	14.0	20.8
Al	2.22	1.24	1.13	2.04
Si	21.5	15.2	16.9	20.5
Ca	2.53	1.33	1.25	2.31
Fe	5.9	27.3	27.5	(9.9)
Minor & Trace (ppm)				
Li	1.9 <sup>c</sup>	2.3	1.7	1.9
F	19	94	32	*1.3
Na	2890	7160	6400	*260
P	65	1750	1080	*(43)
S	200 <sup>h</sup>	(89600)	20000	*(800)
K	230	800	780	*31
Sc	17	8.3	7.9	15.4
Ti	1350	624	600	1220
V	82	81	74	81
Cr	3010	3810	3660	3140
Mn	1020	2850	2320	1310
Co	105	720	810	(220)
Ni	2110	15700	16000	(4720)
Cu	21 <sup>h</sup>	180	82	*(3.3)
Zn	49	450	47	*1.9
Ga	3.8	14.3	6.0	*(0.24)
Ge	1.32	46.9	13	*(0.52)
As(ppb)	150	2670	2050	*(82)
Rb	5409	3170	2900	*120
Mo	59 <sup>d,h</sup>	1330	1700	*(68)
In	18.5	114	11	*0.4
Sn	180 <sup>e,h</sup>	2460	860	*(34)
Sb	5.7	200	70	*(2.8)
Cs	6.8 <sup>g</sup>	260	120	*4.8
W	10 <sup>d</sup>	133	160	(41)
Re	0.24	52	70	(16)
Ir	2.8	700	760	(210)
U	21	11.6	12	19

<sup>a</sup> Wänke et al. (1984) <sup>b</sup> Wasson & Kallemyn (1988) <sup>c</sup> Ryan & Langmuir (1987) <sup>d</sup> Newsom et al. (1986) <sup>e</sup> Jochum et al. (1986) <sup>f</sup> Anders & Grevesse (1989) <sup>g</sup> Hofmann and White (1983) <sup>h</sup> see O'Neill (1991)

the Earth, thus broadly accounting for the identical oxygen isotope patterns in the two bodies. The greater amounts of the other two components in the Moon could allow for some differences, depending on how different their O ratios were from the proto-Earth, which is, of course, not known. There is a 50-50 chance that deviations from Earth-like ratios in these two components would tend to cancel, anyway.

### BULK COMPOSITION OF THE MOON (SILICATE PORTION)

#### Refractory Lithophile Elements

There is general agreement among geochemists that the lithophile refractory elements are present in both the Earth's upper mantle and the Moon in chondritic ratios relative to each other (with the very important exception of V). This is clearly demonstrable for many refractory lithophile trace element ratios (e.g., WÄNKE, 1981; JOCHUM et al., 1986a,b), and it seems fair to assume that this constancy also applies to the major element refractories like Ca, Al, and Ti (e.g., JAGOUTZ et al., 1979; HART and ZINDLER, 1986).

The lithophile refractories appear to be slightly enriched in the Earth's upper mantle relative to Si, by a factor of 1.3, chondrite normalized; this might be due to loss of some Si to the core (e.g., WÄNKE, 1981, and see below), or to a complementary overabundance of Si in the lower mantle (e.g., ANDERSON, 1977; but considered unlikely in the model here), or is simply a compositional peculiarity of the whole Earth. In any event, this only impinges marginally on the matters at hand; the important question is whether the lithophile refractory elements are further enriched in the Moon, relative to Si and Mg. This turn out to be extraordinarily difficult to establish, since there are no lunar analogues of either the spinel and garnet lherzolite nodules, or the Alpine peridotite and ophiolites, which we have as nearly direct samples from the Earth's mantle. The topic has been extensively debated in the literature (e.g., "Earth-like": RINGWOOD, 1979, 1986a; RINGWOOD et al., 1987; WÄNKE, 1981; refractory-enriched: TAYLOR, 1982, 1986a, 1987). The problems and difficulties involved in obtaining any estimate of lunar bulk compositions have been recently discussed by MUELLER et al. (1988) and JONES and DELANO (1989).

Table 2 shows a comparison of the major element composition of the Moon given by the present model (i.e., from

Table 1), with some recent estimates for bulk lunar compositions (without the core). There is good agreement between the present model and the estimates of RINGWOOD et al. (1987) and JONES and DELANO (1989), especially their "equilibrium model" (note that these estimates were obtained from very different methods and assumptions). What small differences there are between these models are mainly due to the different constraints which are assumed; RINGWOOD et al. (1987) assume terrestrial Mg/Si, JONES and DELANO (1989) assume chondritic Mg/Al, whereas the present model differs slightly from either of these two ratios.

There appears to be a significant difference between these "Earth-like" compositions and the refractory-enriched composition proffered by TAYLOR (1982). This is particularly noticeable for CaO and Al<sub>2</sub>O<sub>3</sub>. RINGWOOD et al. (1987) and JONES and DELANO (1989) have both shown that the estimation of such refractory-enriched compositions could result partly from assuming a chondritic Mg/Si ratio. This assumption leads to the following inconsistency: if the Moon really were heavily enriched in the refractory elements, it would probably also have a greater than chondritic Mg/Si ratio, since Si is more volatile than Mg (cf. the CV3 chondrites; WASSON and KALLEMYN, 1988). The other reason for obtaining a high refractory element content is the assumption that the bulk composition of the entire lunar crust is like that of its topmost layer, anorthositic gabbro (Al<sub>2</sub>O<sub>3</sub> 25 wt%). The validity of this assumption is disputable; for example, RYDER and WOOD (1977) have argued that material excavated from deeper down in the crust by large impacts appears noritic (Al<sub>2</sub>O<sub>3</sub> < 20 wt%). Another line of argument used by TAYLOR (1987), which uses the K content of the lunar crust together with the K/U ratio to estimate U (a lithophile refractory element), is equally dependant on this anorthositic view.

Uranium is also the main source of radiogenic heat in the Moon. Early estimates of lunar U from heat flow measurements seemed to indicate a very high abundance of 30–46 ppb (cf. the U abundance of the Earth, 21 ppb). However, the same heat flow data has now been reinterpreted to give only 19 ppb (RASMUSSEN and WARREN, 1985), indistinguishable from the terrestrial value.

Perhaps these different models might eventually prove to be reconcilable; for example, JONES and DELANO (1989) point out that the Taylor refractory-enriched composition could be obtained from the "Earth-like" ones merely by the subtraction of ~30% forsteritic olivine. It is possible that such a product of fractional crystallization might exist deep in the lunar interior. This illustrates just how difficult (or impossible) it is to arrive at a model-independent lunar bulk composition. In summary, there is disagreement on the major element composition of the Moon, but the majority view now seems to favour an Earth-like composition, Fe-enriched. The model presented here produces just such a composition. Note that normalized to the model value of 20.5% Si, the lunar abundances of the refractory lithophile elements should be 1.25 CI.

Finally, it may be noted that any (slight) deviations from a strictly chondritic composition in parts of the proto-Earth's mantle, caused, for instance, by crystal fractionation from a magma ocean, could be inherited by the Moon; in the Earth

Table 2. Composition of the Moon (silicate portion): a comparison of models for the major elements.

Oxide (wt %)	This model	Jones & Delano (1989)		Ringwood et al. (1987)	Taylor (1982)
		Equilibrium model	Fractional Crystal. model		
MgO	35.1	37.1	38.7	36.9	32.0
Al <sub>2</sub> O <sub>3</sub>	3.9	3.7	3.9	3.7	6.0
SiO <sub>2</sub>	44.6	42.6	44.0	43.2	43.5
CaO	3.3	3.0	3.1	3.0	4.5
FeO	12.4 <sup>a</sup>	13.6	10.0	12.2	13.0
Na <sub>2</sub> O	0.05	---	---	0.06	0.09
TiO <sub>2</sub>	0.17	0.19	0.18	0.3	0.3
Cr <sub>2</sub> O <sub>3</sub>	0.47	---	---	0.32	---
MnO	0.17	0.19	0.12	0.16	---
Mg#	0.83	0.83	0.87	0.84	0.81

<sup>a</sup> after subtracting 0.5% Fe to the lunar core

these inhomogeneities would probably then be destroyed by the mixing in of the material returned in the aftermath of the impact. This type of model thus provides a ready mechanism for explaining small deviations from strictly chondritic refractory lithophile element ratios in the bulk Moon (e.g., Sm/Nd or Lu/Hf) should further investigation require this.

**Volatile Elements**

HOFMANN and WHITE (1983) have demonstrated that the volatile lithophile elements Rb and Cs are closely correlated with the refractory Ba in terrestrial MORBs and OIBs. Figure 1 shows that a similarly good correlation of Rb with Ba exists in the Moon and that, relative to Ba, Rb is considerably more depleted in the Moon. A best fit by eye gives a mean Rb/Ba ratio of 0.024, or 0.025 CI; assuming Ba is present in the Moon at 1.25 CI/Si, this gives a depletion of Rb relative to CI and Si of 0.031. This further implies a lunar Rb/Sr ratio of 0.007, in good agreement with most estimates (0.006–0.009; TAYLOR, 1982).

Figure 2 shows an analogous plot of Cs versus Ba. The Cs/Ba ratio in the Moon is indistinguishable from that in the Earth, at 0.014 CI. For K, HOFMANN and WHITE (1983) have shown that this element is not as incompatible as Rb, Cs, or Ba, resulting in a significant slope on a K/Rb vs. Rb diagram. Accordingly, following WÄNKE (1981), I have used the more compatible La as the normalizing refractory element. Potassium/lanthanum is 70, or 0.03 CI. For comparison, Fig. 3 also plots K against U, which actually shows a slightly lower lunar K abundance.

The depletion factors for other non-siderophile volatile elements (largely from RINGWOOD and KESSON, 1977, and WOLF and ANDERS, 1980) are given in Table 3, along with depletion factors for H-group ordinary chondrites, taken from the data of WASSON and KALLEMYN (1988).

A plot of the depletion factors of these elements in the Moon against those in the H-group ordinary chondrites (Fig. 4) shows a good correlation ( $R = 0.99$ ), although in detail

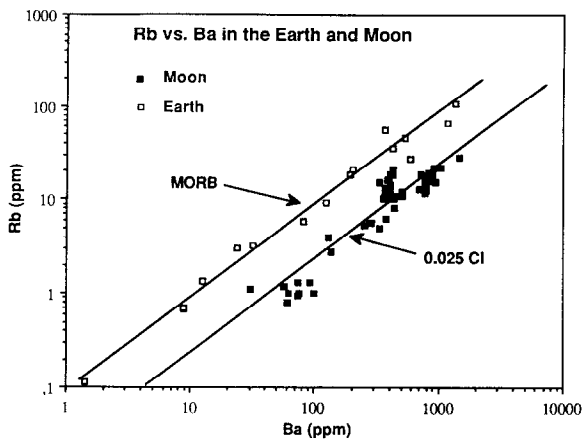


FIG. 1. Rubidium vs. barium in the Earth and Moon. The line labelled MORB is the mean of 166 terrestrial MORBs and OIBs from HOFMANN and WHITE (1983), additional terrestrial data from NEWSOM et al. (1986). Lunar data from CUTTITTA et al. (1973), WÄNKE et al. (1977), PALME et al. (1978), JERDE et al. (1987), SALPAS et al. (1987), and WARREN et al. (1987).

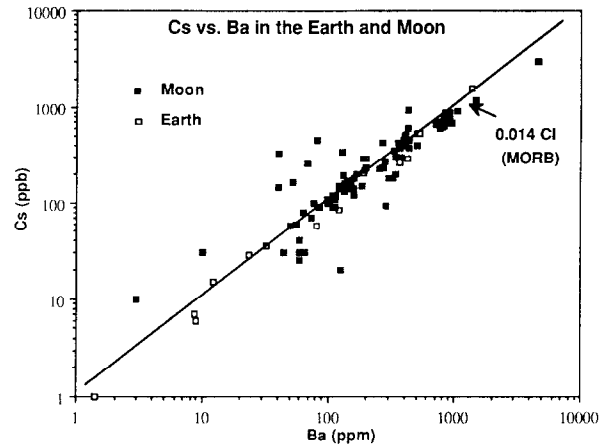


FIG. 2. Cesium vs. barium in the Earth and Moon. The line drawn at Cs/Ba = 0.014 CI is the mean of 166 terrestrial MORB and OIB analyses from HOFMANN and WHITE (1983), points not plotted; other terrestrial data from NEWSOM et al. (1986). Lunar data from TAYLOR et al. (1971), WÄNKE et al. (1977), PALME et al. (1978), MCKAY et al. (1986), JERDE et al. (1987), SALPAS et al. (1987), and WARREN et al. (1987).

the very volatile elements appear more heavily depleted in the Moon, as shown in Fig. 5. This is not significant, as the abundances of these very volatile elements vary considerably with metamorphic type in the ordinary chondrites, and the average values used by WASSON and KALLEMYN (1988) are for the least metamorphosed and, hence, least depleted types. Anyway, the analogy with one particular group of chondrites should not be pushed too far. Also, the determination of the lunar abundances of these very volatile elements is subject to more uncertainty than for the moderately volatile ones.

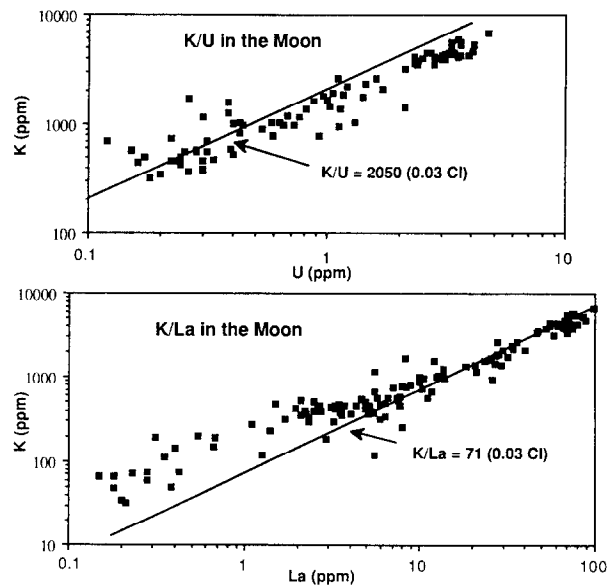


FIG. 3. Potassium vs. lanthanum and potassium vs. uranium in the Moon. The trend towards higher K/La at low (<3 ppm) La results mainly from anorthositic samples and is not significant in the present context. Data from WÄNKE et al. (1977), PALME et al. (1978), LAUL et al. (1983), WARREN et al. (1983), MCKAY et al. (1986), JERDE et al. (1987), SALPAS et al. (1987), and WARREN et al. (1987).

Table 3. Volatile elements in the Moon (non-siderophile or weakly siderophile)

Element	50% Nebular Condensation Temperature(K) <sup>a</sup>	Depletion Moon/CI <sup>b</sup>	Depletion H3/CI <sup>b</sup>	Comments and References
F	740	.012	.31	F/La ~ 0.01 CI. Also (1)
Na	970	.03	.81	Moon/Earth basalts ~0.1(1)
Cl	610	$1.3 \times 10^{-3}$	.073	(1)
K	1000	.037	.87	K/La = 71 (0.03 CI)
Zn	660	$9 \times 10^{-4}$	.093	(1) and (2)
Br	450	$6 \times 10^{-4}$	.086	(2)
Rb	1080	.031	.81	Rb/Ba = 0.024 (0.025 CI)
Ag	650	$2 \times 10^{-3}$	.13	(1) and (2)
Cd	450	$2 \times 10^{-4}$	.016	(1) and (2)
In	480	$10^{-3}$	.085	(1) and (2)
Cs	700	.017	.41	Cs/Ba=0.014 CI
Tl	440	$3 \times 10^{-4}$	.016	(1) and (2)
Pb	520	$7 \times 10^{-4}$	.062	$\mu \sim 300$
Bi	470	$4 \times 10^{-4}$	.096	(1) and (2)

<sup>a</sup> at  $\sim 10$  Pa ( $10^{-4}$  bar). From WASSON (1985) except: Cl - this work - see fig.2; Br - Fegley and Lewis (1980); Ag - assumed to condense with S, not Fe-Ni metal.

<sup>b</sup> Si normalized, assuming 20.5 wt% Si in the Moon.

(1) Ringwood and Kesson (1977)

(2) Wolf and Anders (1980)

What is clear from Figs. 4 and 5 is that the lunar abundances of the well-determined moderately volatile elements may simply be explained by the addition of  $\sim 4\%$  of a component with a composition like that of the H-group chondrites. If the depletion of volatile elements in the Moon had resulted from incomplete recondensation of terrestrial (or any other) material, much more severe fractionation between the most and least volatile elements would have resulted, a point often noted in the past (e.g., WASSON, 1971; WOLF and ANDERS, 1980). Since many of the siderophile elements (volatile or not) are even more depleted in the silicate portion of the Moon, the addition of the 4% volatile-containing fraction must have occurred before the lunar core formed. In fact, meteorite bombardment of the Moon was probably a continuous process throughout its early history, occurring with an intensity which decreased more-or-less exponentially with

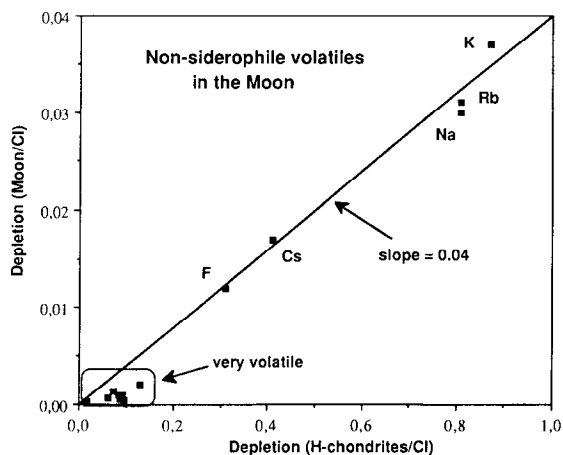


FIG. 4. Volatiles in the Moon: a comparison of the depletion of some non-siderophile (or very weakly siderophile) volatile elements in the Moon with their depletion in H3 ordinary chondrites (from WASSON and KALLEMYN, 1988), both Cl and Si normalized. The abundances of the lunar volatiles may be explained by the addition of  $\sim 4\%$  of an H-chondrite-like component to a volatile-free proto-Moon.

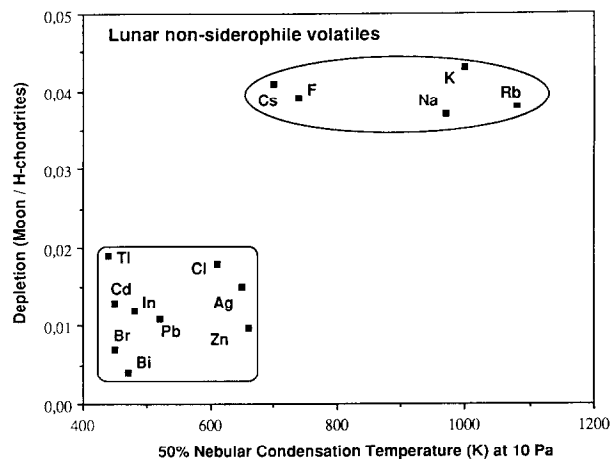


FIG. 5. Volatiles in the Moon: depletion relative to H3 ordinary chondrites (from WASSON and KALLEMYN, 1988) vs. 50% condensation temperature in the solar nebular at  $\sim 10^{-4}$  bar. The 50% condensation temperature for Cl has been calculated from the reaction  $\text{NaCl(g)} + 3 \text{NaAlSi}_3\text{O}_8$  (albite) =  $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{22}\text{Cl}$  (sodalite) + 6  $\text{SiO}_2$ , using new data for sodalite from SHARP et al. (1989). I assume all Cl in the nebula is as  $\text{NaCl(g)}$ , and  $d_{\text{ab}}^{\text{plag}} = 0.4$ .  $T(50\%) = 610$  K at  $10^{-4}$  bar.

time. The record of this bombardment will have only been preserved from such time as when geological activity on the Moon subsided below a certain level, allowing a stable crust to be formed. After this, the ability for metal to segregate to a core will probably cease. From our perspective, then, it is core formation which distinguishes material thought of as being intrinsic to the Moon from that thought of as being merely meteoritic "contamination." The 4% chondritic material may actually be the reducing agent which causes core formation (see below).

Recent support for the hypothesis that the volatiles in the Moon originated from a separate component comes from the study of HINTON et al. (1988) on terrestrial, lunar, and meteoritic K isotopes. Terrestrial K is isotopically heavier than that in meteorites, as would be expected if K in the Earth had been depleted by volatility-related fractionation. However, despite the Moon being even more depleted in K than the Earth (by a factor of 7), lunar K is isotopically lighter than terrestrial and is in fact similar to meteoritic K. This can really only be explained by the mixing of material devoid (or nearly so) of K with a small fraction of relatively undepleted material, as required in the present model.

CARLSON and LUGMAIR (1988) have identified the lunar ferroan anorthosite 60025 as a possible example of early formed lunar crust, with an ancient age of  $4.4 \pm 0.02$  Ga. The extremely low Rb in this rock allows them to identify a very precise initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, which indicates unambiguously that lunar Sr evolved from 4.55 Ga in an Rb/Sr environment considerably more depleted in Rb than chondritic, yet rather less depleted than the bulk Moon (in fact, an environment like that of the bulk Earth, in agreement with the present model).

KREUTZBERGER et al. (1986) have pointed out that the Cs/Rb ratio in the Moon is higher than that in the Earth, despite the greater volatility of Cs compared to Rb and the other alkalis. In the context of the type of model presented here,

this observation has no significance as to whether the Moon formed largely from terrestrial material, since in the Moon, both Cs and Rb are derived entirely from the late stage component. Actually, comparing the ratios of two volatile elements confuses matters. Figures 1 and 2, in which Rb and Cs are compared against Ba, clearly show that it is not Cs which is enriched in the Moon relative to the Earth, but Rb which is less depleted in the Earth. In the present model, this is explained by the proto-Earth containing a small amount of Rb (also Na and K), but having lost (or failed to accrete) virtually all of its highly volatile Cs.

### Volatile Siderophile Elements

Accepting this two-component hypothesis as the explanation of the Moon's abundances of the lithophile volatile elements enables the total amounts of the volatile siderophile elements expected in the bulk Moon (silicate portion plus core) to be deduced. These amounts are simply 4% of the H-chondrite abundances, if the element concerned is sufficiently volatile for none of it to be inherited from the proto-Earth or Impactor. This, of course, begs the questions of which elements are volatile, and to what extent, since the material condensing to the proto-Moon will do so under physico-chemical conditions very different from those in the solar nebula, or those under which the chondrites formed and were metamorphosed. Therefore, the sequence of elemental depletions due to volatility as seen in, say, the ordinary chondrites (which correlates reasonably well with the sequence of calculated 50% condensation temperatures from the solar nebula; WAI and WASSON, 1977) cannot necessarily be used to infer which of the siderophile elements are refractory and which are volatile, without further calculation. Specifically, during the formation of the Moon:

- 1) The chemical composition of the vapour will be very much more depleted than the solar nebula in diverse highly volatile elements such as H (especially), N, Cl, and S, which often form stable gaseous molecules with the other elements of interest here. Hence, elements whose volatility depends on such molecules will tend to become more refractory (e.g., P; FEGLEY and LEWIS, 1980; and Ga; WAI and WASSON, 1979).
- 2) Oxygen fugacities are likely to be much higher (probably between IW and QFM + 2—see Appendix 2). As a result, some elements normally thought of as refractory may become volatile (Mo?), and vice versa.
- 3) Partial pressures of most moderately volatile elements are likely to be lower than in the solar nebula at temperatures near their condensation (see Appendix 2), so that elements which tend to form polyatomic gaseous molecules (e.g., P, As) may become relatively more refractory.

A key element in understanding the role of condensation/volatilization processes in the formation of the Moon is Li, as it is the most volatile of the refractory lithophile elements (cf. DREIBUS et al., 1976). The systematics of the trace element chemistry of Li in terrestrial basalts and mantle peridotites has been discussed by RYAN and LANGMUIR (1987), whose results will be accepted here. It may be noted that the semi-compatible behaviour of Li leads to more complicated

behaviour during igneous differentiation than that shown by the very incompatible elements like K, U, Rb, etc., discussed above. Hence, due care must be exercised in the interpretation of element/element correlations.

RYAN and LANGMUIR (1987) recommend a primitive mantle abundance of  $1.9 \pm 0.2$  ppm, giving a terrestrial depletion factor for Li of 0.58, CI and Si normalised. They also show that Li is empirically correlated with Yb during fractionation in basalts, and found a MORB Li/Yb ratio of 1.7. Figure 6 shows the Li/Yb ratios in various lunar rocks; the mean ratio is indistinguishable from the terrestrial MORB ratio, suggesting that the abundance of Li is the same in the Moon as in the Earth, and thus, within the framework of the present model, that the net depletion of Li in the Moon relative to chondritic is inherited from the Earth, with Li behaving as a refractory element in the Moon-forming process. By contrast, the Li/Yb ratio is about 5 in eucrites and howardites (data from PALME et al., 1978, and DREIBUS and WÄNKE, 1980), indicating that Li is not depleted from chondritic in the EPB. This is of particular significance given the low Moon-like abundances of the other alkali elements (Na, K, Rb, and Cs) in the EPB.

We may use the twin observations that Li is fully condensed (or nearly so), while Na is fully volatilised (or, likewise, nearly so), during the formation of the proto-Moon, as constraints to bracket the condensation behaviour of other elements. Details of the calculations are given in Appendix 2. The pertinent results, which are unfortunately not always conclusive, are summarised as follows:

- 1) Mn—relatively more refractory than Li under all likely conditions;
- 2) Cr—may become slightly volatile under the most oxidising conditions feasible;
- 3) W and Mo—may be volatile, Mo much more likely so than W;
- 4) Ga—may become at least partially refractory;
- 5) P, Cu, Ge, Sn, In and probably As and Sb—volatile under all likely conditions.

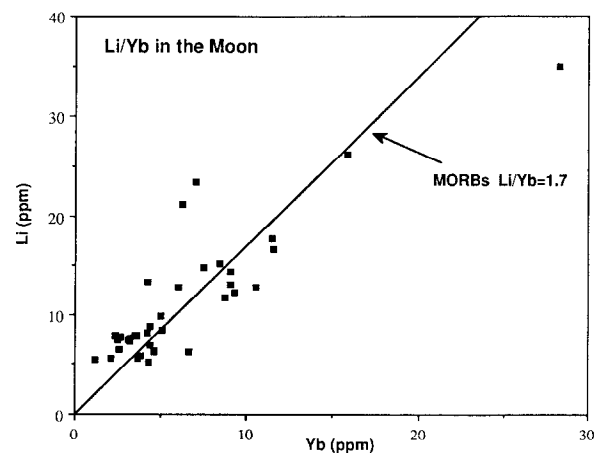


FIG. 6. Lithium in the Moon. The terrestrial MORB Li/Yb correlation ( $Li = 1.7 Yb$ ) is from RYAN and LANGMUIR (1987). Lunar data from CUTTITTA et al. (1973), WÄNKE et al. (1977), PALME et al. (1978), and SHEARER et al. (1990), using Er for Yb (not usually analysed).



## SIDEROPHILE ELEMENTS IN THE MOON-SILICATE PORTION

### Iron, Nickel, and Cobalt

Lunar Mg#’s (defined as molar Mg/Mg + Fe) are constrained not only by the petrology of lunar samples, but also by geophysical properties, such as density (e.g., WOOD, 1986, Mg# = 0.84) and seismic velocities (e.g., HOOD, 1986). A synthesis by MUELLER et al. (1988) gives 0.78 for the lunar upper mantle only. Recent petrological estimates include 0.81 (TAYLOR, 1986b), 0.84 (RINGWOOD et al., 1987), 0.82–0.84 (JONES and DELANO, 1989), and 0.87–0.91 (WARREN, 1986). The latter estimate is from the more problematical highland basalts. The solar (chondritic) Mg# is 0.544 (ANDERS and GREVESSE, 1989), and that of the Earth’s upper mantle is 0.89 (Table 1). From a broad perspective, then, the Moon is like the Earth’s mantle in being very depleted in Fe, although in detail the lunar mantle has a significantly higher FeO content. A lunar Mg# of 0.83 was selected and used to constrain the ratio of terrestrial mantle to chondritic material in the Moon.

DELANO (1986) has used a range of “pristine” lunar mare glasses (including the Green Glasses) to estimate that the primitive silicate portion of the Moon contains  $470 \pm 50$  ppm Ni. Delano further deduces a Co content of  $90 \pm 5$  ppm, giving a Ni/Co ratio of 5. Similar Ni abundances were obtained by WOLF and ANDERS (1980), and Ni and Co abundances by WÄNKE and DREIBUS (1986), RINGWOOD and SEIFERT (1986), and SEIFERT et al. (1988). These estimates represent a depletion of Ni in the source regions of the mare basalts relative to the Earth by a factor of 3–5, and of Co by  $1.05 \pm 0.10$  (DELANO, 1986) to 1.7 (WÄNKE and DREIBUS, 1986). The latter estimate was obtained from a direct comparison of the Co/(Mg + Fe) ratios in lunar and terrestrial basalts. Correcting to allow for higher lunar FeO would bring this estimate into even closer agreement with Delano, which is, therefore, the one adopted.

DELANO and RINGWOOD (1978) inferred similar lunar Ni and Co abundances from their reconstruction of the magma parental to the lunar highlands. However, many “pristine” highland samples contain far less Ni. WÄNKE et al. (1978) pointed out that these rocks commonly originated from magma bodies slowly cooled in the lunar crust, where they would be likely to precipitate metal by autoreduction (e.g.,  $2 \text{Cr}_{\text{sil}}^{2+} + \text{Ni}_{\text{sil}}^{2+} = 2 \text{Cr}_{\text{spinel}}^{3+} + \text{Ni}_{\text{metal}}^0$ ). The siderophile element contents of such rocks will be severely depleted and are obviously not a good reflection of the lunar mantle. In contrast, the only feasible ways of enriching a lunar rock in Ni are by meteorite contamination or the addition of fractionally crystallized olivine. The former is commonly corrected by assuming that all Ir in a sample comes from meteoritic contamination, and that this meteoritic component had chondritic Ni/Ir. The latter operation, olivine accumulation, has been invoked by TAYLOR (1987) and NEWSOM and TAYLOR (1989) to suggest that lunar Ni contents determined from the mare basalt suite, green glasses, etc., are too high, because these rocks were produced from a cumulate enriched source. Specifically, TAYLOR (1987) states “the low-Ti lunar glasses, in contrast to basalts from the terrestrial upper mantle, come from a cumulate region, where Ni is

expected to be enriched. Accordingly, this value of Ni for the silicate portion of the Moon is likely to be overestimated by a factor of two.” This ignores the fact that the Ni estimate comes from the comparison of the lunar and terrestrial correlations of Ni with MgO, which will automatically take any olivine accumulation into account. For example, terrestrial analogues of this proposed mechanism of Ni enrichment by olivine accumulation are probably provided by the olivine-enriched picrites and komatiites, or, albeit less directly, by the boninites and related low-Ti basalts, which are usually reckoned to be produced from already heavily depleted and, hence, olivine- and Ni-rich mantle (e.g., HAMLYN et al., 1985). Such rocks are indeed Ni-rich; but they also have high MgO contents and plot exactly on the terrestrial trend of DELANO (1986). Actually, the easiest way to test the olivine cumulate hypothesis is to consider what effect it would have on the Mg#’s of the mare basalts and green glasses. Olivine-liquid Ni-Mg distribution coefficients,  $K_{\text{Ni-Mg}}^{\text{ol-liq}}$ , are greater than unity, while  $K_{\text{Fe-Mg}}^{\text{ol-liq}}$  is less (e.g., 1–3 and 0.28–0.33, respectively; TAKAHASHI, 1978); consequently any process involving olivine fractionation which raises Ni must at the same time reduce Fe. The involvement of orthopyroxene will exacerbate matters, as this phase does not concentrate Ni, while still reducing Fe. Thus, any process doubling the Ni content of the mare basalt source region will result in lowering considerably its Fe content. The mare basalt source region is consistent with a Mg# of 0.83, or less; therefore, if this source region is enriched over the bulk Moon in Ni, it must also be depleted over the bulk Moon in Fe. This would imply absurdly Fe-rich bulk lunar silicate compositions. It would appear that NEWSOM and TAYLOR (1989) are less than convinced by their own thesis, as they seem to have used the DELANO (1986) Ni estimate, or something near it, themselves (see their Fig. 2).

### Other Siderophile Elements in the Moon

The moderately siderophile elements include W and Mo (usually considered to be refractory, but which may become volatile under oxidising conditions), Ga (vice versa?), and P, As, Sb, Cu, Sn, and Ge (volatile). With the exception of Ge, all these elements are more or less incompatible (see Table A1 in Appendix 1). The lunar abundances of these elements are given in Table 4, together with their depletion factors in the lunar mantle relative to that of the Earth. These abundances were obtained in two ways:

- 1) Compare the ratios of the element of interest with a refractory lithophile element of similar compatibility, whose abundance is taken as the model ideal (i.e., 1.3 times CI for the Earth, 1.25 CI for the Moon). Examples of such ratios are W with U (RAMMENSEE and WÄNKE, 1977), and P with Nd (WÄNKE and DREIBUS, 1986);
- 2) Compare the mean abundances in terrestrial vs. lunar basalts, and then normalise this ratio to the terrestrial mantle abundance (RINGWOOD and KESSON, 1977; WOLF and ANDERS, 1980); note that this implicitly assumes that both types of basalts are generated by similar degrees of partial melting.

For elements with variable valency, both approaches suffer from the flaw that the typical valence state in basalts may

Table 4. Siderophile elements in the Moon - a summary.

Element	Primitive Lunar Mantle	Ratio Earth/Moon Mantles	Method and References
P	20 (ppm)	3±1	P/Nd (Ref. 1) - but see Wänke & Dreibus (1986)
Co	90	1.05±0.1	Delano (1986) - see text
Ni	470	4±0.5	Delano (1986) - see text
Cu	2.1	9	lunar/terrestrial basalt = 9 (Ref. 2) *
Ga	660 (ppb)	5±2	Ga/Al, Warren & Kallemyr (1984) also Ref. 2 and Drake et al (1984)
Ge	6	200	Refs. 2 and 3
As	1	160	Ref. 2
Mo	2.2	27±20	Mo/Nd (Ref. 1)
Sn	6	30	45±20 ppb in low Ti mare basalt - Ref. 3
	30	6	220 ppb, Sn/Eu = 0.2±1 Taylor et al. (1971)
Sb	10 <sup>-2</sup>	500	Ref. 2 - but Ref.3 reports a relative Earth/Moon depletion of only 17
W	11	0.9	W/U = 0.52, Palme & Rammensee (1981)
	18	0.6	(W/U) <sub>Moon</sub> /(W/U) <sub>Earth</sub> = 1.8, Wänke & Dreibus (1986)

References: 1 Newsom (1986); 2 Ringwood & Kesson (1977); 3 Wolf & Anders (1980)

\*  $c_{\text{Cu}}^{\text{Moon's mantle}} = c_{\text{Cu}}^{\text{lunar basalt}} / c_{\text{Cu}}^{\text{terrestrial basalt}}$ ,  $c_{\text{Cu}}^{\text{Earth's mantle}}$ , corrected for residual sulfide,  $c_{\text{Cu}}^{\text{Earth's mantle}} = 18.5 \text{ ppm}$  - see Appendix 1 of O'Neill (1991)

differ between the oxidized environment of the Earth and the reduced environment of the Moon, thus maybe causing marked changes in geochemical behaviour. For example, in the Earth Ge occurs as  $\text{Ge}^{4+}$ , in which state it substitutes readily for Si in silicates, making it very compatible. In reduced environments Ge seems to occur in silicate melts as  $\text{Ge}^{2+}$  (SCHMITT et al., 1989), which will make it less compatible. This might explain the greater dispersion of Ge abundances in lunar basalts relative to terrestrial noted by MALVIN and DRAKE (1987). Similarly, if sulfide is a residual phase during basalt genesis in the Earth (or if sulfide has fractionated from the basalts), terrestrial chalcophile elements will be systematically underestimated (see Appendix 1 in O'NEILL, 1991).

### THE MOON'S CORE

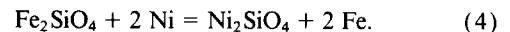
H-group ordinary chondrites contain 27.5% Fe, of which about 80% occurs either as metal or sulfide. Therefore, the addition of 4% of such material to a proto-Moon with negligible oxygen buffering capacity should result in the Moon having a net metal content of ~0.9%. This is the proposed size of the lunar core on an S-free basis. Consequently, both the reduced oxidation state of the lunar mantle and the approximate size of the lunar core may be accounted for by addition of such material.

Although the aim of this paper is to discuss the *chemistry* of the Earth-Moon relationship, it is necessary to adopt a view on how core formation *physically* occurs, so that appropriate parameters can be assumed for the chemical arguments. In what follows, I assume conditions which lead to the simplest model for the chemistry: that metal segregation took place in one episode from an homogenous Moon, after all the reducing material had accreted, and under conditions of chemical equilibrium. I assume a temperature of 1300°C, sufficiently high to ensure substantial partial melting of the

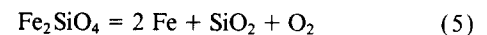
lunar surface (the magma ocean); this is probably a necessary prerequisite for the segregation of small amounts of metal. 1300°C is also the temperature at which much of the relevant experimental work on metal-silicate equilibria has taken place. The effect of pressure is ignored, as it only reaches 57 kbars at the center of the Moon, anyway. Obviously, this view is an oversimplification; nevertheless, it may be justified for now by noting that the errors so introduced are almost certainly going to be less than the uncertainties in the available metal/silicate partitioning data, let alone the accuracy to which lunar abundances are known. Eventually, though, it must be recognised that simple chemical models have a limit to their accuracy; for example, metal segregation might have taken place in a number of batches, at a variety of temperatures, from a proto-Moon that was never fully homogenised, etc. An alternative model, in which metal separation to the core is pictured to occur continuously and contemporaneously with accretion (i.e., analogous to fractional crystallization) was tested, but will not be further pursued. The main effect of this model is to predict a slightly smaller (~0.7%), more Ni-rich, lunar core.

### Oxygen Fugacity—The Olivine-Orthopyroxene-Metal Equilibrium

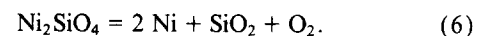
The equilibrium partitioning of Fe and Ni between olivine and metal may be represented by the reaction



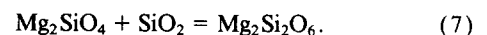
In turn, this equation may be thought of as being the sum of the two constituent equations



and



Either equilibrium (5) or (6) may be used to calculate the oxygen fugacity at which an olivine of known composition is in equilibrium with Fe-Ni metal, provided that the activity of silica ( $a_{\text{SiO}_2}$ ) is known. In planetary mantles this constraint is supplied by the presence of orthopyroxene, which defines  $a_{\text{SiO}_2}$  through the reaction



For example, using Eqn. (5):

$$\log f_{\text{O}_2} = -\Delta G_{(5)}/2.3 RT + \log a_{\text{Fe}_2\text{SiO}_4}^{\text{ol}} + \log a_{\text{SiO}_2} + 2 \log a_{\text{Fe}}^{\text{met}}. \quad (8)$$

The three-phase assemblage olivine-orthopyroxene-metal is completely defined at any given pressure and temperature in the five-component system MgO-SiO<sub>2</sub>-Fe-Ni-O, if two suitable compositional parameters are specified (e.g., the Mg/Fe ratio of the olivine, and the Fe/Ni ratio in either the olivine or the metal). If both ratios are known, the  $f_{\text{O}_2}$  is uniquely determined. This is just the statement of the phase rule for this particular situation. This simple five-component system is actually quite a good model for real planetary mantles, provided that there are no extra incompatible siderophile elements (for example S, but perhaps others such as P) present

in sufficient amounts to affect matters. Apart from this, only small amounts of  $\text{Al}_2\text{O}_3$  (with perhaps some  $\text{Cr}_2\text{O}_3$ ) in the orthopyroxene are likely to be of any quantitative significance, and these may easily be shown to have only a very minor effect on  $a_{\text{SiO}_2}$ , through equilibrium (7).

The thermodynamic data needed for the calculation of  $f_{\text{O}_2}$  as a function of the composition of olivine and metal in the  $\text{MgO-SiO}_2\text{-Fe-Ni-O}$  system are summarized in Table 5; these data have been critically discussed in SEIFERT et al. (1988) and O'NEILL and WALL (1987). The results of the calculation at  $1300^\circ\text{C}$  and 1 bar are displayed in Figs. 7 and 8, which shows the composition ( $\text{Ni}/(\text{Ni} + \text{Fe})$ ) of the metal, and the  $f_{\text{O}_2}$  of the equilibrium, respectively, plotted against the mole fraction of  $\text{Ni}_2\text{SiO}_4$  in the olivine, for different mole fractions of  $\text{Fe}_2\text{SiO}_4$  in olivine. For the inferred primitive lunar olivine composition ( $X_{\text{Fe}_2\text{SiO}_4} = 0.17$  and  $X_{\text{Ni}_2\text{SiO}_4} = 0.001$ , which corresponds to 775 ppm Ni in olivine), the equilibrium defines  $\log f_{\text{O}_2}$  equal to  $-11.6$  at  $1300^\circ\text{C}$ , some 0.8 log-bar units below the iron-wüstite (IW) buffer, which is in agreement with other estimates of lunar  $f_{\text{O}_2}$  (BVSP, 1981, pp. 375–376). This  $f_{\text{O}_2}$  will be used, at  $1300^\circ\text{C}$ , for subsequent calculations. Most redox equilibria have slopes in  $\log f_{\text{O}_2}$  vs.  $1/T$  space that are at least sub-parallel to each other, so that, as a first-order approximation, changing  $T$  will not change the  $f_{\text{O}_2}$  relative to IW, or grossly shift other partitioning relations.

The composition of the Ni-Fe metal in equilibrium with this olivine is calculated to be 48% Ni. SEIFERT et al. (1988) noted that the calculation tended to overestimate slightly the amount of Ni in the metal compared to their experiments; taking this into account, I adopt a value of 45% Ni. SEIFERT et al. (1988) also showed that Ni-Fe exchange between olivine and metal is moderately sensitive to temperature (e.g., see their Fig. 1). However, it is unlikely that core formation in the Moon would take place at temperatures outside of the broad range  $1100\text{--}1700^\circ\text{C}$ , so that the Ni content of the lunar core is almost certainly constrained to lie between about 35 to 55% Ni. Adopting either extreme would have only slight effects on the arguments which follow. The work of SEIFERT et al. (1988) also shows that the exchange of Ni and Co between olivine and metal is insensitive to temperature; Ni and Co are also compatible elements, so that their siderophile properties will not be greatly affected by the amount of partial melt assumed to be present. Consequently, the Ni/Co ratio in the Moon provides a good test of metal fractionation models.

Table 5. Summary of thermodynamic data needed for calculation of the olivine-orthopyroxene-metal equilibrium in the system  $\text{Mg-Si-Fe-Ni-O}$ .

Reactions:		Reference
$2 \text{Fe} + \text{SiO}_2 + \text{O}_2 = \text{Fe}_2\text{SiO}_4$	$-564.8 + 0.1444 T$ kJ/mol	O'Neill (1987a)
$2 \text{Ni} + \text{SiO}_2 + \text{O}_2 = \text{Ni}_2\text{SiO}_4$	$-485.7 + 0.1792 T$ kJ/mol	O'Neill (1987b)
$\text{Mg}_2\text{SiO}_4 + \text{SiO}_2 = \text{Mg}_2\text{Si}_2\text{O}_6$	$6710 + 0.31 T$ J/mol	O'Neill and Wall (1987)
<b>Activity coefficients:</b>		
$(\text{Fe-Mg})_2\text{SiO}_4$ (regular solution)	$W_{\text{Mg-Fe}}^{\text{ol}} = 5000$ J/g-atom	O'Neill and Wall (1987)
$\text{Ni}_2\text{SiO}_4$ (Henry's Law)	$\gamma_{\text{Ni}}^{\text{ol}} = 1.03$ (per cation)	Seifert and O'Neill (1987)
Fe-Ni (subregular solution)	$W_{\text{Fe-Ni}}^{\text{ol}} = -5740$ J/mol	Fraser and Rammensee (1982)
	$W_{\text{Ni-Fe}}^{\text{metal}} = -13290$ J/mol	
$\text{Mg}_2\text{Si}_2\text{O}_6$	Ideal (Raoultian)	

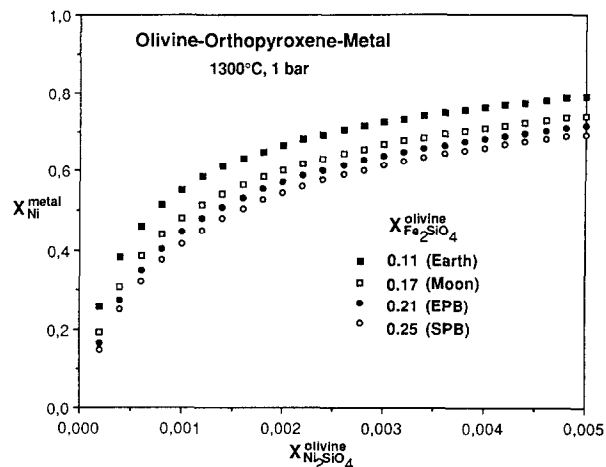
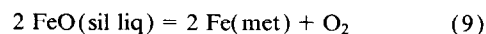


FIG. 7. Composition of the metal in equilibrium with olivine and orthopyroxene in the system  $\text{Fe-Ni-Mg-Si-O}$  at  $1300^\circ\text{C}$  and 1 bar, plotted as a function of the Ni content of the olivine, for different  $\text{Mg}/(\text{Mg} + \text{Fe})$  in olivine.

Much previous modelling of the effects of a small lunar core on the net siderophile element content of the Moon has used a somewhat lower  $f_{\text{O}_2}$  than that argued for here; i.e., 2 log-bar units below IW (NEWSOM and DRAKE, 1983; DRAKE et al., 1984). This estimate comes from the equilibrium



for the condition where a silicate melt with the FeO content of the bulk silicate Moon (13 wt%) is in equilibrium with pure Fe metal. There are thus two more-or-less equally important reasons why this estimate is too low.

- 1) Neglect of Ni in the metal. This results in  $f_{\text{O}_2}$  values too low by  $2 \log a_{\text{Fe}}^{\text{met}}$  or 0.5 log-bar units.
- 2) The assumption that the FeO content of the silicate melt during metal segregation is that of the bulk Moon.

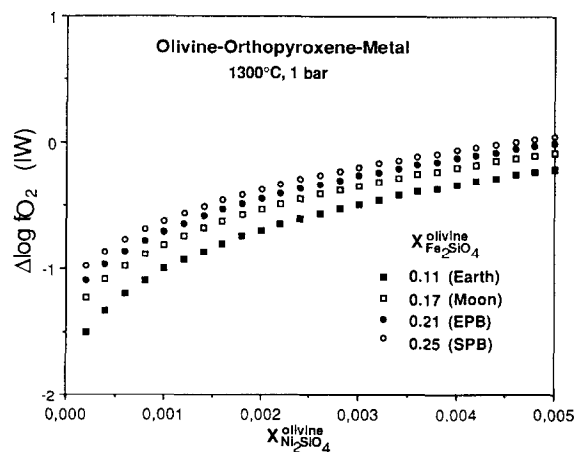


FIG. 8. Oxygen fugacity defined by the olivine-orthopyroxene-metal equilibrium, in log-bar units, relative to the Fe-“FeO” (IW) oxygen buffer.

Any likely lunar composition would not be completely molten at the temperatures assumed for metal separation ( $\sim 1300^\circ\text{C}$ ), and, indeed, most such modelling has very reasonably gone on to assume low degrees of silicate partial melting for this process. A more appropriate FeO content for a lunar partial melt near  $1300^\circ\text{C}$  (and about 20% melt fraction) would be  $\sim 20\%$ , as for primitive mare basalts or the green and brown glasses. Adoption of this figure raises the  $f_{\text{O}_2}$  calculated with this approach by a further 0.4 log-bar units, bringing it into good agreement with the estimate from olivine-orthopyroxene-metal used here.

Recently NEWSOM and TAYLOR (1989) have published the opinion that "an argument against Ni-rich metal in equilibrium with lunar silicates comes from the very reduced oxidation state of the Moon. . . . If lunar silicates had equilibrated with Ni-rich metal, lunar oxygen fugacities would be much higher." The above calculations demonstrate that this unsubstantiated conjecture is simply not true. Ni-rich metal is actually observed in some mare basalts (HEWINS and GOLDSTEIN, 1974).

### The Role of Sulfur

The amount of S which would be added to the Moon by the 4% H-chondrite component is  $\sim 800$  ppm. If all but, say, 100 ppm (a rough estimate of the amount left in the source regions of the Mare basalts) of this is removed to the core, the S content of the lunar core would be  $\sim 8\%$ . This is nearly the amount of S in metal-saturated Fe-Ni-S metallic liquid at  $1300^\circ\text{C}$  at  $\text{Ni}/\text{Ni} + \text{Fe} = 0.45$  (HSIEH et al., 1987). HSIEH et al. (1987) also show that at high temperatures the Ni/Fe ratios of coexisting solid and S-containing metallic liquids are nearly the same, and, of course, under these conditions  $a_{\text{Fe}}$  and  $a_{\text{Ni}}$  in the liquid must be the same as that in the solid metal. Thus, there is no need to modify the above olivine-metal calculations.

There are a couple of advantages in supposing that the lunar core contains S. Firstly, the metal being molten when the core formed will have aided segregation. Secondly, a molten (or partly molten) core acting as a dynamo might explain the remanent magnetization of lunar rocks, some as young as 3.1 Ga. To assume a lunar core of molten S-free, Fe-Ni metal implies excessively high temperatures in the lunar interior, such as would only be attainable if the silicate portion of the Moon were also to be still substantially molten, which is impossible at this late stage of its history (HOOD, 1986). This point was made by BRETT (1973), who proposed a core made of near eutectic Fe-Ni-S alloy. The composition proposed here is poorer in S than the (pseudo-) eutectic, which, incidentally, occurs at S contents near 30% for  $\text{Ni}/\text{Ni} + \text{Fe} = 0.45$ , at a temperature below  $900^\circ\text{C}$  at 1 bar (HSIEH et al., 1987). If the Moon's core is indeed poorer in S than the eutectic composition, then, although it might have been molten initially, cooling of the Moon's interior will have resulted in its progressively freezing, shutting down the lunar dynamo at some point in the past; there is no magnetic field on the Moon today. Nevertheless, most proposed selenotherms for the modern Moon predict a temperature at its center substantially above  $900^\circ\text{C}$ , so some portion of the core should still be liquid. These speculations would be quite testable, if seismic monitoring on the Moon were to be recommenced.

### Iron, Nickel, and Cobalt

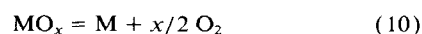
The chondritic Mg# is 0.544, the lunar Mg# is  $\sim 0.83$ ; therefore, if a chondritic abundance is assumed for the non-volatile siderophile elements, the material that formed the Moon must have lost about 75% of its initial Fe, somewhere in its history. If this loss had occurred by metal fractionation, it would have also stripped this material of virtually all Ni, yet the Ni content of the Moon is at least 470 ( $\pm 50$ ) ppm, even without taking a possible Ni-rich lunar core into account. This situation may be compared to that pertaining in the silicate part of the Eucrite Parent Body, in which the geochemical signature of metal fractionation is clear, and which has a silicate Ni content of only 40 ppm (DREIBUS and WÄNKE, 1980). This is less one tenth of the lunar abundance, and, moreover, the EPB is less FeO depleted; DREIBUS and WÄNKE (1980) give a Mg# of  $\sim 0.79$ .

Consider now the consequences for lunar siderophile element chemistry if the Moon formed out of material with siderophile abundances like that of the terrestrial upper mantle. To obtain the depletion in Ni by a factor of 4, which is inferred from the mare basalts, would need the removal of 0.4% metal with 40% Ni (RINGWOOD and SEIFERT, 1986); this would cause a concomitant reduction of Co in the mare basalt source by a factor of  $\sim 2$  compared to the Earth's mantle, assuming 1.2% Co in metal (SEIFERT et al., 1988)—rather more than the estimate given by DELANO (1986) of  $1.05 \pm 0.10$ . Separation of 0.4% Ni-rich metal would hardly affect the abundances of the moderate siderophiles like W and P, which would, therefore, be just slightly depleted over their terrestrial abundances (approximately consistent with observation), but would be capable of drastically depleting the highly siderophile elements like the Pt group elements, Re, Mo, and Ge (again as observed). However, as well as the Co discrepancy, this model also cannot explain the rather higher FeO in the lunar mantle (TAYLOR, 1987; NEWSOM and TAYLOR, 1989).

The present model gives a total lunar abundance of Ni of 4720 ppm. The primitive lunar mantle abundance is 470 ppm, in equilibrium with metal with  $\text{Ni}/\text{Ni} + \text{Fe} = 0.45$ . The lunar core is then constrained to be 0.9% of the lunar mass, neglecting S. Including S brings this up to 1%, a conveniently round figure which is adopted for subsequent calculations. If this core contains 1.2% Co (as experimentally determined for solid Ni-rich, S-free metal by SEIFERT et al., 1988), the calculated bulk lunar Co abundance is  $90 + 120 = 210$  ppm, in excellent agreement with the predicted amount of 220 ppm. The empirical evidence from the magmatic iron meteorites indicates that the liquid metal/solid metal distribution coefficient for Co is near unity (e.g., MALVIN et al., 1984), so this conclusion is not likely to be adversely affected by the presence of some S in the Moon's core.

### The Siderophile Trace Elements

The partitioning of a siderophile element M between a metal phase and a silicate melt may be represented by the reaction



so that at chemical equilibrium

$$\ln X_M^{\text{met}} = \ln X_{\text{MO}_x}^{\text{sil liq}} - \ln \gamma_M^{\text{met}} + \ln \gamma_{\text{MO}_x}^{\text{sil liq}} - \Delta G_{(10)}^0/RT + x/2 \ln f\text{O}_2. \quad (11)$$

The empirical solid metal-silicate melt distribution coefficient,  $D_M^{\text{sol met/sil liq}}$ , is then given by

$$D_M^{\text{sol met/sil liq}} = c_M^{\text{met}}/c_M^{\text{sil liq}} = k \exp[-\Delta G_{(10)}^0/RT + x/2 \ln f\text{O}_2 - \ln(\gamma_M^{\text{met}}/\gamma_{\text{MO}_x}^{\text{sil liq}})], \quad (12)$$

where  $\gamma_{\text{MO}_x}^{\text{sil liq}}$  and  $\gamma_M^{\text{met}}$  are the thermodynamic activity coefficients of  $\text{MO}_x$  and M in the silicate liquid and Fe-Ni alloy, at infinite dilution for trace elements.  $k$  is a constant to convert from mole fractions to ppm. Experimentally,  $D_M^{\text{sol met/sil liq}}$  has typically been measured as a function of  $f\text{O}_2$  (either explicitly or by varying the FeO content of the silicate melt) at some chosen temperature (often 1300°C and 1600°C) for a representative melt composition and a metal composition which has usually had a rather low Ni/Fe ratio than that required here. Consequently, the values of  $\gamma_{\text{MO}_x}^{\text{sil liq}}$  and  $\gamma_M^{\text{met}}$  appropriate to the specific conditions for core formation in the Moon may vary somewhat from the experimental values, introducing additional uncertainties into the calculation.

The present model also assumes that the core-forming metal in the Moon is a S-containing liquid, and consequently the distribution coefficient of interest is  $D_M^{\text{liq met/sil liq}}$ , which may be related to the usual quantity experimentally determined,  $D_M^{\text{sol met/sil liq}}$ , by

$$D_M^{\text{liq met/sil liq}} = D_M^{\text{sol met/sil liq}} * D_M^{\text{liq met/sol met}}. \quad (13)$$

$D_M^{\text{liq met/sol met}}$  has been measured for a few elements, albeit at lower Ni/Fe ratios than desirable. For some other elements (e.g., Co, Cu, As, Sb), empirical evidence for liquid metal/solid metal partitioning behaviour may be gleaned from the variation in their abundances in the magmatic iron meteorites (such as Group IIIAB), the chemistry of which is thought to have evolved by fractional crystallization of molten metal (SCOTT, 1972). For example, the small variation of Ga and Ge with Ni in these meteorites indicates  $D_M^{\text{liq met/sol met}}$  close

to that for Ni, just greater than unity, whereas the five-fold variation in Sb may be explained by  $D_{\text{Sb}}^{\text{liq met/sol met}}$  near 2.3 (WAI and WAASON, 1979).

The concentration of element M in the silicate melt is

$$c_M^{\text{sil liq}} = c_M^{\text{sil}}/[1/D_M^{\text{sil liq/sil sol}}(1-f) + f] \quad (14)$$

where  $f$  is the mass fraction of partial melt,  $c_M^{\text{sil}}$  is the total concentration of M in the silicate (solid plus melt, i.e., here the primitive lunar mantle), and  $D_M^{\text{sil liq/sil sol}}$  is the Nernst bulk distribution coefficient between the solid silicate (and oxide) phases and the melt.  $D_M^{\text{sil liq/sil sol}}$  generally depends on the chemistry and structure of the melt and what the solid phases and their compositions are, as well as temperature, pressure, and oxygen fugacity. An attempt to estimate  $D_M^{\text{sil liq/sil sol}}$  under conditions of planetary differentiation (albeit in the Earth), for a wide variety of elements, has been made in Appendix 1, and numerical values are given in Table A1.  $f$  is not an independent variable, but at constant pressure it is completely determined by the bulk composition of the system and the assumed temperature. For 1300°C at low to moderate pressures in the Moon,  $f$  should be about 20% (certainly in the range 10–35%; see, e.g., MCKENZIE and BICKLE, 1988, their Fig. 6), and this value is adopted.

The concentration of M in the metal phase in equilibrium with the primitive lunar mantle is then

$$c_M^{\text{met}} = c_M^{\text{sil}} * D_M^{\text{liq met/sol met}} * D_M^{\text{liq met/sol met}} / [1/D_M^{\text{sil liq/sil sol}} * (1-f) + f], \quad (15)$$

and therefore the bulk concentration in the Moon (primitive mantle plus core) is

$$c_M^0 = c_M^{\text{met}} m + c_M^{\text{sil}}(1-m) \quad (16)$$

where  $m$  is the fractional mass of the lunar core, taken here to be 1%.

Primitive lunar mantle abundances of some siderophile elements are summarised in Table 4. Some of these estimates are of considerable uncertainty—as indicated, for example,

Table 6. Critical summary of siderophile trace element partitioning relationships between silicate liquid, solid metal and S-containing liquid metal.

Element	$D_M^{\text{sol met/sil liq}}$ 1300°C -11.6 log fO <sub>2</sub>	References	$D_M^{\text{liq met/sol met}}$ (8% S; default value is 1)	References	Adopted $D_M^{\text{liq met/sil liq}}$	Primitive Lunar Mantle	Calculated Bulk Moon (Eqns. 15 & 16)
P	1-3	1, 3	5-10	9, 10	20	20 (ppm)	36 (ppm)
Cu	27	1, 2	1¶	11	27	2.1	3.5
Ga	5-6	1, 4, 5	1	9	5	660 (ppb)	750 (ppb)
Ge	600-2000 (1000)	1, 2	1	9	3000#	6	210
As	(1000)	13	5¶	11	1000	1	35
Mo	200-1000	1, 4, 6	?		1000	2.2	75
Sn	20-35	2, 7	?		34	6-30	14-70
Sb	(1200)	13	2.3¶	12	1200	10 <sup>-2</sup>	0.6
W	4-6	1, 4	0.5	9	3	11-18	13-21

References: 1 Schmitt et al. (1989); 2 Seifert (1987), also Seifert and Ringwood (1987); 3 Newsom and Drake (1983); 4 Rammensee (1978); 5 Drake et al. (1984); 6 Kor (1984); 7 Rankin (1986); 8 Rammensee and Wänke (1977); 9 Jones and Drake (1983); 10 Malvin et al. (1986); 11 Malvin et al. (1984); 12 Wai and Wasson (1979); 13 Klöck and Palme (1988), empirical data, includes  $D_M^{\text{liq met/sol met}}$  correction.

¶ estimated from magmatic iron meteorite systematics. # adjusted by 1.5 for  $\gamma_{\text{Co}}^{\text{met}}$  at Ni/(Fe+Ni) = 0.45, ternary subregular model, binary alloy data from Erdelyi et al. (1977, 1978) and Fraser and Rammensee (1982)

by the alternate values, where given. Selected experimentally or empirically determined values for  $D_M^{\text{sol met/sil liq}}$  at 1300°C and  $\log f_{\text{O}_2} = -11.6$ , and  $D_M^{\text{liq met/sol met}}$ , are given in Table 6. Equations (15) and (16) may be used to calculate the whole Moon abundances of the incompatible siderophile elements from their inferred abundances in the primitive lunar mantle, subject, of course, to all the uncertainties discussed above. The model for the origin of the Moon may then be tested by comparing these abundances with those calculated from the mass balance in Table 1, as set out in Table 7.

There is good agreement between model and calculated values for Cu and P. The low Mo abundance of the Moon can only be explained if this element is volatile, implying condensation under oxidising conditions (Appendix 2). For W, an element which has received much attention in the lunar origins debate (e.g., RAMMENSEE and WÄNKE, 1977; WÄNKE and DREIBUS, 1986), calculated values are about half that of model ones. This is a degree of agreement which may be considered fairly satisfactory given all the uncertainties, but which might be improved further if W becomes partially volatile (oxidising conditions again). Alternatively, W being a highly incompatible element (Appendix 1), a match could be achieved with  $f = 2\%$  rather than the 20% adopted here.

The model seems to underestimate Ga by a factor of three, but here again improvement results if Ga becomes partially refractory, as predicted for oxidising conditions. The poorly constrained abundances of the indubitably volatile siderophiles Ge, As, Sb, and Sn are all within a defensible range of model values. The depletion of P into the lunar core (probably also As and Sb) depends on the presence of S in the metal to raise the metal/silicate partition coefficient.

### The Highly Siderophile Refractory Elements

The highly siderophile (or noble metal) refractory elements are Ru, Rh, Pd, Re, Os, Ir, Pt, and maybe Au (the latter may be slightly volatile). The bulk lunar abundances of these elements is given by 26% CI (volatile free) plus 4% H-chondrite in the present model, so that they should be present in chon-

dritic proportions relative to each other. Their relative depletions in the lunar mantle should then simply follow their metal/silicate distribution coefficients, corrected for compatibility. There is some evidence for this (e.g., Re and Ir; NEWSOM, 1986). The observed abundances of these elements would potentially be able to test further the present model, but only usefully if the product of the metal/silicate distribution coefficient times the lunar silicate abundance, corrected both for compatibility and for the S content and Ni/Fe ratio of the metal, is known to better than an order of magnitude. This is certainly not the case at present. The lunar abundances of these elements are particularly difficult to determine because their intrinsically low levels are swamped by any late stage meteoritic contamination. In addition, very little is known of their high temperature petrochemical properties.

### THE V-Cr-Mn CONTROVERSY

Vanadium, chromium, and manganese are a triplet of elements which are siderophile under very reducing conditions (or could perhaps become so). They have received considerable attention in the lunar origins debate because (a) their planetary abundances can be determined quite accurately, and (b) these abundances show similar levels of depletion in the Earth's upper mantle and the Moon (e.g., RINGWOOD et al., 1987; DRAKE et al., 1989), but not, for example, in the Eucrite Parent Body or the SNC meteorites (WÄNKE and DREIBUS, 1986). The available metal/silicate partition coefficients (RAMMENSEE et al., 1983; DRAKE et al., 1989) show that V and Cr would barely be affected by metal fractionation in the Moon, and Mn not at all; consequently, their observed lunar abundances should simply be inherited from the material out of which the Moon accreted. Explanations that the similar abundances reflect depletion by volatility, and are, therefore, due to similar processes in the solar nebula and not to derivation of this material from a terrestrial-like source, flounder on the fact that while Cr and particularly Mn do indeed appear to be slightly volatile under nebula conditions, V is clearly not (WÄNKE, 1981). Vanadium correlates with the refractory elements in every chondrite group (WASSON and KALLEMYN, 1988) and is also enriched along with the other refractories in Ca, Al-rich chondrules from the Allende meteorite (WÄNKE, 1981; KORNACKI and FEGLEY, 1986). Its calculated 50% condensation temperature from the solar nebula is above Mg and Si (WASSON, 1985, pp. 250–252) and is very similar to the rare earth Yb (1542 vs. 1549 at  $10^{-3}$  bars; KORNACKI and FEGLEY, 1986).

Vanadium is also present in refractory hibonite-bearing grains from the Murchison CV chondrite (IRELAND et al., 1988). These grains show marked volatility-related fractionation among the normally refractory lithophile trace elements, for example, in the REEs, between Er (very refractory) and Yb (comparatively volatile). In Fig. 9, I have plotted the ratio V/Sc (Sc is a very refractory trace element which behaves geochemically quite similarly to  $V^{3+}$ ) against Yb/Er. There is a good correlation between these pairs, extending over 4 orders of magnitude, which empirically confirms the similar volatility of V to Yb. There is no hint of a Yb anomaly in the Moon; consequently, one should not expect lunar V to be depleted by volatility either.

Table 7. Siderophile elements in the Moon - summary and comparison

Element	Calculated Bulk Moon	This Model	CI normalised to 20.5% Si	present Earth's mantle
Fe	9.9 (%)	9.9	36.8	5.9
P*	36 (ppm)	43	2360	65
V	93	81	109	82
Cr	2300	3140	5140	3010
Mn	1250	1310	3844	1020
Co	210	220	970	105
Ni	4500	4720	21000	2110
Cu*	3.5	3.3	240	21
Ga*	750 (ppb)	240	19000	3800
Ge*	210	520	63000	1320
As*	35	82	3600	150
Mo*	75	68	1800	59
Sn*	14-70	34	3300	180
Sb*	0.6	2.8	270	5.7
W	13-21	41†	180	10

\* Volatile † 9 ppb if W is volatile

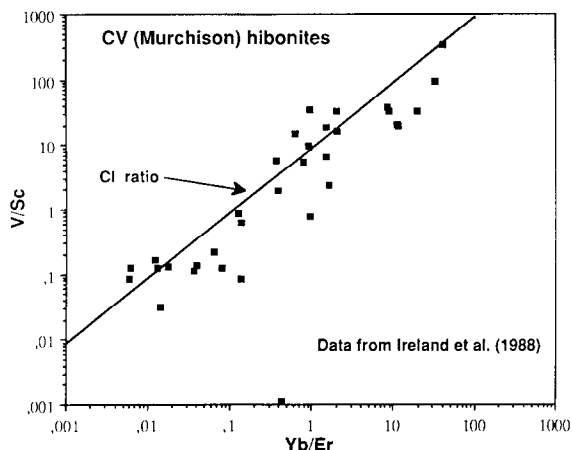


FIG. 9. Vanadium/scandium vs. ytterbium/erbium in hibonites from refractory inclusions in the Murchison CV3 chondrite. There is an excellent correlation between the depletion (by volatility) of V and Yb. Data from Ireland et al. (1988).

The thermodynamic calculations on volatility discussed earlier also present the paradox that while Cr might become more volatile than Li at very oxidising conditions, Mn will only do so when extremely reduced.

The point is sometimes made that the depletion of V, Cr, and Mn in the Earth and Moon is in the order of their increasing volatilities (e.g., NEWSOM and TAYLOR, 1989). While this might be true in a sophisticated sort of way, it obscures the fact that V is a refractory element in the usual cosmochemical sense of the term and is less volatile than Mg or Si; hence, the situation may be more fairly appreciated by considering the larger set V, Mg, Si, Cr, and Mn together.

#### Lunar Abundances of V, Cr, and Mn

An excellent correlation between MnO and FeO in a large variety of lunar samples (highland rocks and soils, and low Ti-Mare basalts) was demonstrated by LAUL et al. (1974), who obtained  $\text{MnO}/\text{FeO} = 0.013$ . This is in precise agreement with the  $\text{MnO}/\text{FeO}$  ratio given by the present model (0.014), assuming, as argued in Appendix 2, that Mn behaves as a refractory element during lunar formation. Since this particular ratio is perhaps the surest known of all items of lunar chemistry, the ability of the present model to accurately reproduce it may be accorded particular significance.

The  $\text{MnO}/\text{FeO}$  ratio in the Earth's mantle is 0.017 (Table 1). However, since the Moon is about 50% richer in FeO than the Earth's mantle, the absolute Moon/Earth Mn ratio is predicted to be 1.3; that is, the Moon is less depleted in Mn than the Earth. This is in quantitative agreement with the conclusions reached by DRAKE et al. (1989), who obtain  $\text{Mn}_{\text{Moon}}/\text{Mn}_{\text{Earth}} = 1.36 \pm 0.14$ . Their estimate is virtually the same as an earlier one by RINGWOOD and KESSON (1977).

A detailed account of the lunar chemistry of Cr and V has recently been given by SEIFERT and RINGWOOD (1988). For the lunar highland breccias, SEIFERT and RINGWOOD (1988) show that correlations almost as good as the one between MnO and FeO may be obtained between CrO and FeO, and VO and FeO. The reason for the close geochemical coherence

of all these elements during igneous differentiation in the Moon is that, under the low  $f\text{O}_2$  values prevailing in the lunar environment, most Cr and presumably also much V occur in the divalent state in silicate melts (see also SCHREIBER and HASKIN, 1977) as, of course, do Fe and Mn. Furthermore, all these elements have similar cation radii in the divalent state, with the natural result that they all possess rather similar olivine/liquid, orthopyroxene/liquid and even clinopyroxene/liquid partition coefficients, as experimentally demonstrated by RINGWOOD and SEIFERT (1986; V is a bit different from the others). Only with the involvement of spinel (which concentrates Cr and V) is this coherence expected to break down.

SEIFERT and RINGWOOD (1986) obtained lunar  $\text{CrO}/\text{FeO}$  and  $\text{VO}/\text{FeO}$  ratios of 0.024 and  $9.9 \times 10^{-4}$ , respectively. With the model value of 12.4% FeO for the lunar mantle (Table 2), these ratios yield Cr = 2300 ppm and V = 93 ppm. A variety of more sophisticated methods of estimation used by SEIFERT and RINGWOOD (1986), some independent of the particular lunar mantle FeO content adopted here, give essentially the same answers (2190–2463 ppm Cr and 79–95 ppm V). Similar abundances were also deduced by DRAKE et al. (1989).

The lunar abundance of V is within the likely uncertainty of the model abundance (81 ppm; Table 1) and is considerably less than the abundance of 140 ppm expected, if V behaved like the other refractory lithophile trace elements, present at 1.25 times CI levels, Si normalised. This difference would, of course, become greater if the Moon is refractory enriched.

The estimated Cr abundance (2300 ppm) is rather less than the model abundance of 3140 ppm (Table 1) and very much less than the Si-normalised chondritic abundance of  $\sim 5000$  ppm. It is difficult to account for this in any way other than by postulating that some Cr might have been lost from the accreting Moon by reason of its enhanced volatility under oxidising conditions. The conditions necessary would be in accord with the partially volatile behaviour for W, and the complete volatility of Mo.

#### ORIGIN OF THE MOON—A SUMMARY

The calculated abundances of the siderophile and related elements discussed above for the integral bulk Moon (i.e., primitive mantle plus core) are given in Table 7, where they may be compared to the abundances predicted by the present model, and also with chondritic (Si normalised) and the present Earth's mantle abundances.

The above discussion has focussed on the evidence offered by the siderophile element abundances in the Moon, because it is on a few of these—the refractory ones—that the unique signature of the Moon's terrestrial provenance is imprinted. Others behave as volatile elements, which, I have argued, are not inherited from the Earth. Below is a brief summary of, firstly, how well both the abundances (lunar mantle) and properties (siderophile and volatile) of these elements are known, and, consequently, the weight which should be accorded to each in assessing the merits of the model; and secondly, how well these inferred abundances agree with the model:

- 1) Fe, Ni—used to constrain the model. An independent test would be the size of the lunar core.
- 2) Mn, V, Co—abundances and behaviour very well known, accurately predicted.
- 3) Cr—abundance well known, but is about 25% less than predicted—could be explained if assumed to be slightly volatile.
- 4) Cu, P—behaviour reasonably well known, abundances probably estimated to  $\pm 50\%$ , accurately predicted.
- 5) W, Ga—behaviour and abundances reasonably well known (to about a factor of 2), fair agreement with model.
- 6) Ge—abundance well known, behaviour less so. Accounted for fairly well by the model within these limits.
- 7) Mo, Sn, As, Sb—abundances only moderately or poorly known, behaviour poorly known. Mo must behave as a volatile to agree with the model.
- 8) Pt group, Au, Re—more work needed.

A comparison of the model bulk Moon composition with that inferred for the primitive lunar mantle plus core is shown in Fig. 10. There appears, at present, satisfactory agreement between model and observation for the siderophile elements. This is somewhat remarkable considering the simplistic view taken on the timing and mechanism of core formation, the temperature and degree of partial melting at which this occurred, etc. Other aspects of lunar chemistry for which the present model accounts reasonably well are the similarity of O isotopes to those of the Earth, the pattern of the volatile element depletion, and the K isotopes anomaly.

How well do other models account for these inferred whole Moon abundances? Firstly, the kind of two-component model used here to explain the volatile element abundances in the Moon may also be adapted to other scenarios, so that the volatile siderophile elements cannot really be used as effective discriminants. This leaves the two triplets, Fe, Ni, and Co, and V, Cr, and Mn, with possibly W, as the elements worth arguing about. A strictly chondritic siderophile element abundance pattern (Table 7) is ruled out by the undoubted depletion in Fe of the Moon, deduced from density consid-

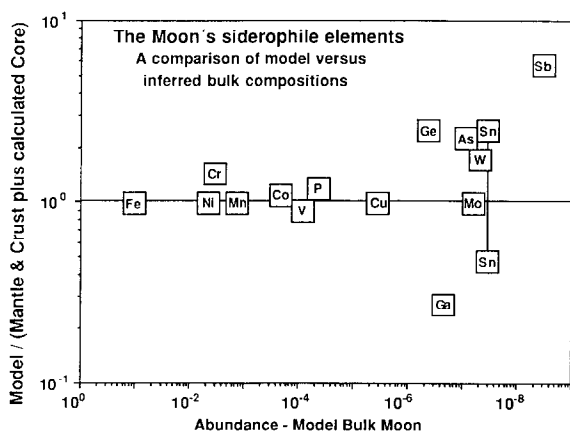


FIG. 10. Siderophile elements in the Moon—a comparison of the three-component model bulk composition (proto-Earth + Impactor + late veneer) with the inferred bulk composition of mantle (and crust) plus the 1% Ni-rich core. Possible ranges for the uncertain elements Ge and Sn are indicated (see text for details).

erations (WOOD, 1986), and, compared to this, to mention any other constraint (e.g., W abundances, V-Cr-Mn depletions) is gilding the lily.

A more viable hypothesis is derivation of the Moon from the Earth's mantle (e.g., RINGWOOD, 1986a,b, 1989a; WÄNKE and DREIBUS, 1986; also reviewed by DRAKE, 1986, 1987). The two chief arguments against this are (a) if the Co abundance of DELANO (1986), adopted here, is right, then any core required to produce the depletion of the primitive lunar mantle in Ni will result in a net (silicate plus core) Co content which is too high (e.g., by a factor of 2, argued above); and (b) the higher FeO content of the Moon. JAGOUTZ and WÄNKE (1982) have suggested that this objection may be overcome if the Moon separated from the Earth's mantle before core formation in the Earth is complete (e.g., DELANO and STONE, 1985); whatever process is envisaged for the way in which core formation is completed (e.g. disproportionation of FeO), it could hardly remove Fe from the mantle without having a much larger effect on the other more siderophile elements, especially Ni. Thus, material derived from an incompletely differentiated, FeO-richer Earth mantle cannot be invoked to account for the bulk Moon's resemblance in Ni and Co to the present day Earth's mantle. I would like to emphasise, though, how important to the testing of these models more geophysical information on the size and nature of the lunar core would be.

NEWSOM and TAYLOR (1989) have suggested that the Moon is largely derived from the Impactor and that the depletion of the siderophile elements in the bulk Moon (including a lunar core) can be explained by prior core formation in the Impactor. This implies that the pattern of depletion, shown here and elsewhere (e.g., WÄNKE and DREIBUS, 1986; RINGWOOD, 1989a) to be Earth-like, is due to processes which are not unique to the Earth. Whether this is likely, or not, can only be judged if these processes are understood. In the following paper (O'NEILL, 1991), I shall argue that the siderophile pattern in the Earth's mantle comes from the special circumstances associated with impact event and is most unlikely to have arisen independently in a Mars-sized body. Hence, most of the Moon must have come from the Earth.

*Acknowledgments*—I would like to thank Carl Agee and many other colleagues at the Bayerisches Geoinstitut, as well as Horton Newsom and, in particular, Ted Ringwood for reading and commenting on the first version of this manuscript. My intellectual debt to Ted should be obvious. I am also very grateful for the extensive, careful, and fair-minded formal reviews by Paul Warren and John Jones, which resulted in a slimmer and, I hope, more readable product, as well as eliminating some of my sillier flights of fancy. Sympathetic editorial handling by Paul Hess and Gunter Faure is also appreciated.

*Editorial handling:* P. C. Hess

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## APPENDIX 1

## An Empirical Compatibility Scale

The "compatibility" of a trace element is a measure of its tendency not to partition into a silicate partial melt. Incompatible elements do not substitute readily into the major solid phases of a planetary mantle and so are concentrated into a partial melt, if one is present. As a result, their chemical potential and, hence, their siderophile or volatile properties depend on the degree of melting. The ratio of the

concentration of a trace element,  $M$ , in a partial melt over that in the residual solid phases with which the melt is in equilibrium defines the distribution coefficient

$$D_M^{\text{liq/sol}} = c_M^{\text{liq}}/c_M^{\text{sol}}, \quad (\text{A1})$$

where the bulk concentration of the element, is given by

$$c_M^0 = c_M^{\text{liq}} \cdot f + c_M^{\text{sol}} \cdot (1 - f) \quad (\text{A2})$$

and  $f$  is the fraction of the melt. This leads to the equation for trace element distribution during equilibrium melting:

$$\frac{c_M^{\text{liq}}}{c_M^0} = \frac{1}{1/D_M^{\text{liq/sol}} + f \cdot (1 - 1/D_M^{\text{liq/sol}})}. \quad (\text{A3})$$

For a very incompatible element,  $D_M^{\text{liq/sol}} \gg 1$ , so it may usually be assumed that all the element resides in the melt, provided that the melt fraction is not excessively small. The exact value of  $D_M^{\text{liq/sol}}$  is, therefore, not important. However, for elements of intermediate incompatibility, the concentration of the element in the melt and, hence, its chemical potential and siderophile tendencies will vary sensitively with  $D_M^{\text{liq/sol}}$ .

In principle, a suitable average value for  $D_M^{\text{liq/sol}}$  may be calculated at a given  $T$  and  $P$ , if individual  $D$  values are known for each solid phase, together with the modal proportions of these phases; for example,

$$D_M^{\text{liq/sol}} = D_M^{\text{liq/ol}} \cdot Z_{\text{ol}} + D_M^{\text{liq/opy}} \cdot Z_{\text{opy}} + D_M^{\text{liq/cpx}} \cdot Z_{\text{cpx}} + D_M^{\text{liq/grt}} \cdot Z_{\text{grt}} + D_M^{\text{liq/matte}} \cdot Z_{\text{matte}}, \quad (\text{A4})$$

where  $Z_\phi$  is the fraction of phase  $\phi$  in the mode. Both the partition coefficients and the modal proportions of the phases will vary as a function of bulk composition and the degree of partial melting, as well as  $T$  and  $P$ . For what is probably a majority of the trace elements of interest in this study, individual mineral/liquid  $D$  values are not known under any conditions.

From this it might seem that the difficulties in accounting for the behaviour of the moderately incompatible elements in any quantitative manner would appear almost insuperable, at least on the scale at which the problem is commonly formulated. However, for modelling planetary processes, we are interested in the mean behaviour of these elements, summed over numerous different local melting conditions—in other words, a planetary average of their incompatibility. For the Earth, just such a compositional average exists in the form of the continental crust, which may be considered to represent a mean fraction of partial melt,  $f_c$ , derived from the primitive Earth's mantle. It is widely accepted from the evidence of isotope and trace element geochemistry that the crust and present-day mantle are complementary to each other, in that the mantle's depletion in the incompatible elements is compensated for by their enrichment in the crust. For many trace elements, HOFMANN (1988) has demonstrated that the relationship is simple but quantitative, and what follows is largely based on his ideas (in a simplified form). The concentration of a trace element,  $M$ , in the crust is assumed to be related to its concentration in the primitive mantle by

$$\frac{c_M^{\text{crust}}}{c_M^{\text{mantle}}} = \frac{1}{1/D_M^{\text{liq/sol}} + f_c \cdot (1 - 1/D_M^{\text{liq/sol}})}, \quad (\text{A5})$$

cf. Eqn. (A3) above. Following HOFMANN (1988),  $f_c$  is taken to be 0.016, implying that the crust has formed (approximately) by differentiation of the upper mantle only (about one third of the whole mantle). This is in agreement with most of the isotope and noble gas evidence (e.g., GALER et al., 1989).

Empirical solid/liquid partition coefficients may then be calculated from Eqn. (A5), using the mantle concentrations given in Table 1 and the composition of the continental crust from TAYLOR and MCLENNAN (1985; their Table 3.5). The results of this exercise are given in Table A1. From Eqn. (A5),  $c_M^{\text{crust}}/c_M^{\text{mantle}}$  tends to  $1/f_c$  when  $D_M^{\text{liq/sol}}$  becomes large; consequently, even within the limitations of all the other assumptions, the method cannot produce meaningful values for the most incompatible elements. As noted above, for most

Table A1. An empirical compatibility scale - Mantle/Crust "silicate liquid/silicate solid" distribution coefficients ( $D_M^{\text{liq/sol}}$ )  
Mantle abundances from table 1, and: refractory lithophile elements = 1.3 Cl/Si; noble metals = 0.5% H-chondrite.  
Crustal abundances from Taylor and McLennan (1985)

Element	$D_M^{\text{liq/sol}}$	Element	$D_M^{\text{liq/sol}}$	Element	$D_M^{\text{liq/sol}}$
Li	8	F	50	Na	9
P	15	K	105	Sc	1.8
Ti	4	V	2.9	Cr	0.06
Mn	1.4	Co	0.27	Ni	0.05
Cu*	4	Zn	1.6	Ga	5
Ge	1.2	As*	7	Rb	(150)
Sr	15	Y	6	Zr	12
Nb	20	Mo*	17	Pd**	0.23
Ag	50	Cd	4	In	2.8
Sn	18	Sb*	80	Cs	(150)
Ba	120	La	42	Ce	30
Pr	21	Nd	16	Sm	10
Eu	8	Gd	7	Tb	7
Dy	6	Ho	6	Er	5.5
Tm	5	Yb	5	Lu	5
Hf	11	Ta	40	W	(150)
Re**	1.4	Ir**	0.03	Au**	3
Pb	(150)	Th	160	U	120

\* possibly (\*\* - almost certainly) too low because of sulfide in the residue.

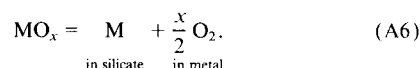
purposes this does not matter, since then  $c_M^{\text{liq}}/c_M^0 \rightarrow 1/f$  anyway. A few very incompatible elements, which seem to be more concentrated in the crust than allowed by this simple model with  $f_c = 0.016$ , have been arbitrarily assigned  $D_M^{\text{liq/sol}} = 150$ , which is given in parentheses.

Partial melting in the Moon will occur under conditions rather different than those of continental crust formation in the Earth—e.g., at lower oxygen fugacities and negligible water pressures. Also, the degree of partial melting at which metal separation in the Moon has been assumed to occur is larger than the average for crust formation. All these factors may effect the compatibilities; nevertheless, in the almost total absence of partitioning data for many elements, the present approach has at least the merits of being systematic.

One interesting point to note are the low values of  $D_M^{\text{liq/sol}}$  for the highly chalcophile elements, Ir (Os and Ru behave similarly) and Pd, and likewise, the lower than expected values for the highly incompatible Re and Au. For example, olivine ( $\pm$ chromite) fractionation in komatiite suites yields  $D_{\text{Ir}}^{\text{liq/sol}} = 0.5$  (BRUGMANN et al., 1987). These apparent anomalies clearly attest to sulfide being a residual phase in the Earth's mantle during the global differentiation processes responsible for producing the continental crust. If something like 100 ppm S is left in the mantle during crust production, elements with sulfide/silicate partition coefficients  $> 10^4$  will be grossly affected; however, the estimated values of  $D_M^{\text{liq/sol}}$  for elements only slightly less chalcophile will also be systematically low, and this might be the reason, for example, why Mo appears so much more compatible than W. There is also a surprising difference between As and Sb, although, of course, such apparent discrepancies may simply be artefacts of the wrong crustal or mantle abundances. Elements thought to be sulfide-affected have been marked by one asterisk (probable), or two (almost certainly). On this evidence Pb does not appear to be significantly chalcophile.

#### Empirical Activity Coefficients for Incompatible Siderophile Elements

The partitioning of an element,  $M$ , between a silicate melt and metal may be written



so that at equilibrium

$$\log a_{\text{MO}_x}^{\text{sil}} = \log a_{\text{M}}^{\text{met}} + \frac{\Delta G(\text{A6})}{2.3RT} + \frac{x}{2} \log f_{\text{O}_2}. \quad (\text{A7})$$

The activity of  $\text{MO}_x$  in the silicate, therefore, depends on the free energy of the reduction reaction, the concentration and activity coefficient of M in the metal,  $x$  (the valence state), and the oxygen fugacity.

Taking the standard state of  $\text{MO}_x$  to be the pure oxide in its stable form at the temperature of interest, we may define an empirical activity coefficient,  $\lambda_{\text{MO}_x}^{\text{sil liq}}$ , for  $\text{MO}_x$  in silicate melts, such that

$$a_{\text{MO}_x}^{\text{sil liq}} = \lambda_{\text{MO}_x}^{\text{sil liq}} \cdot c_{\text{M}}^{\text{sil liq}}. \quad (\text{A8})$$

The activity of M (extrapolated, if necessary, to low dilutions) in the (presumed Fe-rich) metal is taken to be

$$a_{\text{M}}^{\text{met}} = X_{\text{M}}^{\text{met}} \cdot \gamma_{\text{M}}^{\text{met}} = c_{\text{M}}^{\text{met}} \cdot A(\text{Fe})/A(\text{M}) \cdot \gamma_{\text{M}}^{\infty, \text{met}}. \quad (\text{A9})$$

The results of experimental investigations of metal/silicate liquid distribution coefficients are customarily given in the form

$$\log D_{\text{M}}^{\text{met/sil liq}} = \log c_{\text{M}}^{\text{met}}/c_{\text{M}}^{\text{sil liq}} = A + B \log f_{\text{O}_2}, \quad (\text{A10})$$

where  $A$  and  $B$  are the experimentally determined constants. If  $B$  equals  $x/2$ , then comparing Eqns. (A7), (A8), and (A9) with (A10) shows that

$$\log \lambda_{\text{MO}_x}^{\text{sil liq}} = A + \log \gamma_{\text{M}}^{\infty, \text{met}} + \log A(\text{Fe})/A(\text{M}) + \frac{\Delta G(\text{A6})}{2.3RT}, \quad (\text{A11})$$

where, on account of the choice of standard state,  $\Delta G(\text{A6})$  is the free energy of formation of the oxide in its standard (or any convenient) form at the temperature of interest. This quantity cancels out in use, so its numerical value, and any errors therein, are in practice irrelevant.  $\lambda_{\text{MO}_x}^{\text{sil liq}}$  may then be evaluated if the activity coefficient of M at infinite dilution in Fe-M alloys is known. This  $\lambda_{\text{MO}_x}^{\text{sil liq}}$  will be valid over at least the range of  $f_{\text{O}_2}$  values covered by the partitioning experiments used to deduce  $B$ .

If the coefficient  $B$  cannot reasonably be equated with a suitable  $x/2$  (allowing for some experimental uncertainty in its estimation), which will most likely be due to M existing in more than one valence state, then

$$\log \lambda_{\text{MO}_x}^{\text{sil liq}} = A + \log \gamma_{\text{M}}^{\infty, \text{met}} + \log A(\text{Fe})/A(\text{M}) + \frac{\Delta G(\text{A6})}{2.3RT} + \left( B - \frac{x}{2} \right) \log f_{\text{O}_2}, \quad (\text{A12})$$

Table A2. Empirical activity coefficients for some siderophile elements in silicate melts.  $T = 1573$  K,  $\log f_{\text{O}_2} = -10.7$  (iron-wüstite). Activity coefficients marked with an asterisk may (theoretically) be extrapolated to other  $f_{\text{O}_2}$ 's.

Element	Assumed oxidation state	Standard state	$-\Delta G^\circ$ 2.3 RT	$\log D_{\text{M}}^{\text{met/sil liq}}$	$\gamma_{\text{M}}^{\infty, \text{met}}$	$\lambda_{\text{MO}_x}^{\text{sil liq}}$
			(1)	(2)	(3)	
P	5	1/4P <sub>4</sub> O <sub>10</sub> (g)	13.1	-0.6	10 <sup>-5a</sup>	10 <sup>-5*</sup>
Co	2	CoO(c)	4.1	1.7	1	3
Cu	1	Cu <sub>2</sub> O(l)	0.9	1.1	10	2
Ga	3	1/2Ga <sub>2</sub> O <sub>3</sub> (c)	9.6	-0.1	1(?) <sup>b</sup>	30*
Ge	2	GeO(c)	(4.4) <sup>b</sup>	2.3	0.01 <sup>e</sup>	0.2
Mo	4	MoO <sub>2</sub> (c)	10.3	1.5 <sup>c</sup>	2 <sup>a</sup>	15
	6	MoO <sub>3</sub> (l)	12.8	0.3		10 <sup>-3</sup>
Sn	2	SnO(c)	4.4	1.0 <sup>d</sup>	3	2
W	4	WO <sub>2</sub> (c)	10.3	-0.1 <sup>c</sup>	2 <sup>a</sup>	0.2
	6	WO <sub>3</sub> (c)	14.9	-0.9		5*10 <sup>-3</sup>

(1) Pankratz (1982) (2) from Schmitt et al. (1989), except as indicated.

(3) for liquid alloys. From Hultgren et al. (1973), except as indicated.

<sup>a</sup> Sigworth and Elliot (1974) - estimate for Mo and W. <sup>b</sup> no data - default value

<sup>c</sup> Ramensee (1978) <sup>d</sup> Rankin (1986) <sup>e</sup> Erdelyi et al. (1978)

but the  $\lambda_{\text{MO}_x}^{\text{sil liq}}$  so determined will not be valid at any other  $f_{\text{O}_2}$ . Values of  $\lambda_{\text{MO}_x}^{\text{sil liq}}$  estimated for some siderophile elements of interest in this study are given in Table A2.

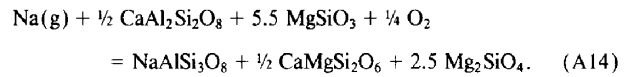
Since at equilibrium, by definition,  $a_{\text{MO}_x}^{\text{sil}} = a_{\text{MO}_x}^{\text{sil liq}}$ , an empirical mean activity coefficient for M in solid silicate may be estimated from

$$\lambda_{\text{MO}_x}^{\text{sil}} = \lambda_{\text{MO}_x}^{\text{sil liq}} \cdot D_{\text{M}}^{\text{sil/liq}}. \quad (\text{A13})$$

## APPENDIX 2

### Volatility of Some Elements under Conditions Appropriate to the Condensation of the Moon

Consider first the condensation behaviour of Na. The vapour/solid equilibrium may be described by the reaction



At equilibrium

$$\log p_{\text{Na}} = \Delta G_{(\text{A14})}^0/2.3RT + \log X_{\text{NaAlSi}_3\text{O}_8}^{\text{plag}} + \frac{1}{4} \log f_{\text{O}_2} \quad (\text{A15})$$

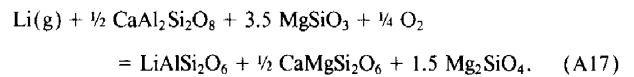
assuming that  $\text{NaAlSi}_3\text{O}_8$  substitutes ideally in plagioclase, and that the activities of the other components are unity (the substitution of  $\text{Fe}^{2+}$  for Mg cancels out across the reaction, so that this is quite a reasonable approximation). The pressure of Na in the vapour is given by

$$p_{\text{Na}} = f_v(c_{\text{Na}}/A_{(\text{Na})}) \cdot k \cdot p_{\text{tot}}, \quad (\text{A16})$$

where  $c_{\text{Na}}$  is the concentration of Na in the material which forms the Moon,  $A_{(\text{Na})}$  is the atomic weight of Na,  $f_v$  is the atomic fraction of Na in the vapour,  $k$  is a normalising constant, and  $p_{\text{tot}}$  is the total pressure of the vapour. Note that vapour/solid equilibria during the Moon-forming process will depend mainly on three thermodynamic variables: temperature, total vapour pressure, and oxygen fugacity.

If all the Na in the protolunar material is condensed,  $X_{\text{NaAlSi}_3\text{O}_8}^{\text{plag}} \approx 0.2$ . An upper limit for the atomic fraction of Na actually condensed may be taken as 2% (which would increase the model abundance of Na in the Moon by  $\sim 20\%$ ), so that  $X_{\text{NaAlSi}_3\text{O}_8}^{\text{plag}} \approx 0.004$ , and  $p_{\text{Na}} = 0.98(c_{\text{Na}}/A_{(\text{Na})}) \cdot k \cdot p_{\text{tot}}$ . These values may be substituted into Eqns. (A15) and (A16) to determine the maximum normalised total pressure ( $k \cdot p_{\text{tot}}$ ) of the vapour at a given temperature and  $f_{\text{O}_2}$ .

Similarly for Li, the condensation reaction may be written



Hence,

$$\log p_{\text{Li}} = \Delta G_{(\text{A17})}^0/2.3RT + \log a_{\text{LiAlSi}_2\text{O}_6}^{\text{sp}} + \frac{1}{4} \log f_{\text{O}_2}. \quad (\text{A18})$$

RYAN and LANGMUIR (1987) found that Li was approximately evenly distributed between all the ferromagnesian phases in terrestrial mantle peridotites. Li probably enters these phases via the coupled substitution  $\text{Li} + \text{Al} = 2 \text{Mg}$  (or  $\text{Fe}^{2+}$ ), so that, assuming ideal mixing,

$$a_{\text{LiAlSi}_2\text{O}_6}^{\text{sp}} \approx X_{\text{LiAlSi}_2\text{O}_6}^{\text{sp}} \approx N_{\text{Li}}/0.5(N_{\text{Mg}} + N_{\text{Fe}}). \quad (\text{A19})$$

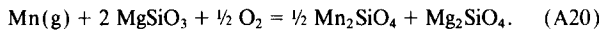
If we then assume that 90% of the available Li is condensed,  $X_{\text{LiAlSi}_2\text{O}_6}^{\text{sp}} = 5 \times 10^{-5}$ , and  $p_{\text{Li}} = 0.1(c_{\text{Li}}/A_{(\text{Li})}) \cdot k \cdot p_{\text{tot}}$ . Thermodynamic data for the phases in reactions (A14) and (A17) may be obtained from ROBIE et al. (1978) and PANKRATZ (1982). These sources were also used for the data needed in the later calculations except where specifically indicated.

Subtraction of Eqn. (A18) from Eqn. (A15) gives an exchange equilibrium between  $\text{Li(g)}$ ,  $\text{Na(g)}$ , and the condensed phases which is independent of  $f_{\text{O}_2}$  and  $k \cdot p_{\text{tot}}$ , but which turns out, conveniently, to be quite sensitive to temperature. The calculation for this reaction shows that the temperature at which condensation ceases must lie below  $\sim 1400$  K; above this temperature the ratio  $p_{\text{Na}}/p_{\text{Li}}$  becomes smaller than the assumed 98/10%-condensed constraints.

Approximate limits to the  $fO_2$  condensation may be deduced from the presumed behaviour of Fe and Ni in the proto-Moon as follows: at the low  $fO_2$  limit there should be no Fe or Ni reduced to metal, so that  $fO_2 > IW$  (the iron-wüstite or Fe- "FeO" oxygen buffer), whereas the high  $fO_2$  limit is set by the requirement that most Fe should exist as  $Fe^{2+}$  and not  $Fe^{3+}$ , otherwise the proto-Moon would have a sufficiently large oxygen buffering capacity to cancel out the reducing effect of the 4% late stage component.  $fO_2$  must also be less than  $p_{tot}$ . This limits the  $fO_2$  to below 1–2 log-bar units above the QFM buffer. These temperature and oxygen fugacity conditions may then be used to test other elements to see if they are either more volatile than Na, or more refractory than Li, during the formation of the proto-Moon. The results for some critical elements will now be discussed.

### Manganese

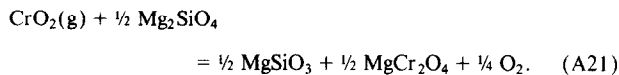
The vapour/solid equilibrium may be represented by the reaction



The free energy data for  $Mn_2SiO_4$  are given by ROBIE et al. (1982). I assume that monatomic Mn(g) is the only important vapour species. Hence, Mn becomes increasingly refractory as  $fO_2$  increases, proportionally to  $(fO_2)^{1/2}$ , compared to only  $(fO_2)^{1/4}$  for Li and Na. The calculation shows that, for the limit set by 90% condensation of Li, Mn will be about 99% condensed at 1400K and  $fO_2 = IW$ , and becomes even less volatile at lower temperatures and higher  $fO_2$ . Thus, Mn behaves as a refractory element during the formation of the proto-Moon. Similarly, the gaseous monoxides of the divalent siderophiles Fe, Ni, and Co are not particularly stable (PEDLEY and MARSHALL, 1983), so that these elements will also show increasing relative refractoriness with increasing  $fO_2$ , and are, thus, also expected to be completely condensed.

### Chromium and Vanadium

Unlike Mn, Cr has a number of known and reasonably stable oxide gas species— $CrO(g)$ ,  $(CrO_2)_2(g)$ , and  $CrO_3(g)$ . Whereas the monatomic gas,  $Cr(g)$ , is the most abundant species in the solar nebula (FEGLEY and PALME, 1985), the oxidised species  $CrO_2(g)$  will become dominant at  $fO_2 > IW$  at all relevant temperatures. The condensation of Cr may then be modelled by the reaction

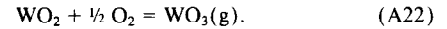


$MgCr_2O_4$  is the major component in spinel, so I assume  $a_{MgCr_2O_4}^{\text{spinel}} = 0.5$ . The thermodynamic data for reaction (A21) shows that Cr will become as volatile as Li at about 1450 K and  $\log fO_2 = QFM + 2$ , and would be more depleted by volatility at higher temperatures and higher  $fO_2$ . These conditions are just outside the limits assumed above to be plausible; however, in view of the uncertainties in the calculations, there must remain the possibility that the Moon may be slightly depleted in Cr by reason of its increased volatility under oxidising conditions. By contrast, the only available thermodynamic data for gas species in the V-O system are for V(g) and VO(g). Of course, absence of data is not proof that more oxidised species might not be stable, but the available evidence indicates that V will remain a completely refractory element.

### Tungsten and Molybdenum

Both these elements have some quite stable oxidised gas species, especially  $WO_3(g)$  and  $MoO_3(g)$ , which will dominate at low vapour pressures at all  $fO_2 > IW$ .

The calculation for the volatile behaviour of W near the IW buffer at 1400 K may be quantified as follows: the metal/silicate melt partitioning experiments of RAMMENSEE and WÄNKE (1977) indicate that W occurs in silicate melts in equilibrium with Fe-rich metal primarily as the tetravalent species, i.e., as  $WO_2$ . The solid/vapour equilibrium may be written



Hence,

$$\log p_w = \Delta G_{(A22)}^0 / 2.3 RT + \log a_{WO_2} + \frac{1}{2} \log fO_2. \quad (A23)$$

I define an empirical activity coefficient,  $\lambda_{WO_2}$ , for  $WO_2$  in the condensed (silicate) material, such that

$$a_{WO_2} = \lambda_{WO_2} \cdot c_w^{\text{sil}}. \quad (A24)$$

$\lambda_{WO_2}$  may be approximately estimated from experimentally measured metal/silicate distribution coefficients, as explained in Appendix 1. I obtain  $\lambda_{WO_2}^{\text{sil}} \approx 0.2$  (at 1573 K, but assumed to be insensitive to temperature); hence,  $\lambda_{WO_2}^{\text{sil}} = \lambda_{WO_2}^{\text{sil}} \cdot D_w^{\text{sil}} \approx 30$ . I assume a negligible melt fraction at 1400 K, so the latter value is adopted. Let the fraction of W left in the vapour be  $f_v$ . Then, from Eqns. (A22), (A23), and the appropriate analogue to (A15),  $f_v$  may be calculated at the presumed normalised vapour pressure at 1400 K and  $IW$ ,  $k \cdot p_{tot} = 2 \times 10^{-5}$  bars, given by the calculated condensation behaviour of Na and Li. The actual expression is

$$\log f_v / (1 - f_v) = -\Delta G_{(A22)} / 2.3 RT + \frac{1}{2} \log fO_2 \\ - \log k \cdot p_{tot} / A_{(w)} + \log \lambda_{WO_2}. \quad (A25)$$

$f_v$  is found to be 0.2%; i.e., W is fully condensed at these conditions, but the calculation is close enough to leave considerable doubt, in view of all the approximations involved. For example, the partitioning experiments of SCHMITT et al. (1989) disagree with those of RAMMENSEE and WÄNKE (1977) in the fairly fundamental respect that they indicate that hexavalent, not tetravalent, W is the dominant species in the silicate melt at 1300°C, in equilibrium with Fe-rich metal. If the above calculation is repeated using the results of SCHMITT et al. (1989), W evinces a slightly more refractory behaviour. Lowering the temperature also tends to make W relatively more refractory, as will the presence of a small melt fraction. Increasing the oxygen fugacity may or may not tend to increase the volatility of W, depending on whether the results of RAMMENSEE and WÄNKE (1977), or of SCHMITT et al. (1989), are accepted. In the former case, it would not be possible to quantify the change on internally consistent information, as increasing  $fO_2$  should also convert  $WO_2$  in the silicate to  $WO_3$ , for which component the activity coefficient would probably be different.

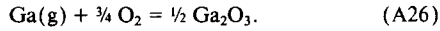
The same calculations for Mo gives  $f_v \approx 50\%$ . Both RAMMENSEE (1978) and SCHMITT et al. (1989) more or less agree that Mo is present in their silicate melts largely as  $Mo^{4+}$ , so Mo is definitely likely to become more volatile with increasing  $fO_2$ . Because Mo also appears to be more compatible than W, the presence of a small melt fraction will not reduce its volatility as much. Hence, Mo is likely to behave at least partially as a volatile element during formation of the Moon. Tungsten and, even more so, molybdenum are commonly depleted relative to other refractory metals in Ca, Al-rich inclusions in carbonaceous chondrites by virtue of their enhanced volatility under relatively oxidizing conditions (FEGLEY and PALME, 1985).

From a thermochemical point of view the more volatile behaviour of Mo vs. W is a result not only of the greater relative stability of  $MoO_3(g)$  vs.  $WO_3(g)$ , but also of the much higher empirical activity coefficient of  $MoO_2$  compared to  $WO_2$  in silicate melts, the factor also responsible for the greater siderophile tendencies of Mo (Appendix 1). Why this should be so is a mystery which must hide some interesting chemistry.

### Gallium

The condensation of Ga in the solar nebula was examined by WAI and WASSON (1979), who concluded that Ga behaved as a volatile element because of the stability of such gaseous molecules as  $GaCl(g)$  and  $GaOH(g)$ , neither of which are likely to be abundant under the conditions assumed for formation of the Moon largely out of the proto-Earth's mantle. The common gas species in the system Ga-O at high vapour pressures is  $Ga_2O(g)$ , which, however, will not occur relative to  $Ga(g)$  at the low total pressures of interest here (thermochemical data from LAMOREAUX and HILDENBRAND, 1987).

GaO(g) is unstable, except at unreasonably high  $fO_2$  (PEDLEY and MARSHALL, 1983). One is forced to conclude that Ga(g) is the dominant vapour species. If so, the solid/vapour equilibrium may be stated as



Thus, Ga becomes more refractory proportionally to  $(fO_2)^{3/4}$  vs. only  $(fO_2)^{1/4}$  for Li. A quantitative calculation, done as for W above, is rendered very uncertain because of an almost complete lack of information on the activity coefficient of Ga in Fe metal. Assuming that it is unity, the calculation indicates that at 1400K and QFM, Ga would be about 25% condensed if Li is 90% condensed. Ga becomes more refractory than Li at lower temperatures along the QFM buffer. If  $\gamma_{\text{Ga}}^{\text{met}}$  is less than unity, (as, for example, assumed by WAI and WASSON, 1979), then Ga would be predicted to become even more refractory. In conclusion, there is the distinct possibility that Ga may behave at least as a partially refractory element during the Moon's formation.

## Others

The volatile behaviour of In closely parallels that of Ga, but In is always considerably more volatile and should have no chance of condensing to the proto-Moon. However, its relatively increased refractoriness under oxidizing conditions may help to explain its surprisingly high abundance in the Earth's mantle.

The volatility of P in the solar nebula depends on such molecules as PN(g) and PS(g). The major volatile species in the P-O system under the conditions of interest here are  $\text{PO}_2(\text{g})$ , with  $\text{PO}(\text{g})$  also becoming important at about the  $fO_2$  of the IW buffer. A calculation similar to that for W above shows that these gaseous oxides are sufficiently stable for P to remain volatile at all likely conditions. Copper, germanium, and tin should also remain volatile, the stable gas species being  $\text{Cu}(\text{g})$ ,  $\text{GeO}(\text{g})$ , and  $\text{SnO}(\text{g})$ . There are insufficient data for a meaningful calculation to be attempted on As and Sb; I assume that they remain volatile.