PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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Phil. Trans. R. Soc. Lond. A 1977 **285**, 55-67
doi: 10.1098/rsta.1977.0043

Phil. Trans. R. Soc. Lond. A. **285**, 55–67 (1977) [55]
Printed in Great Britain

Comparative chemical history of the Earth, the Moon and parent body of achondrite

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Chronological studies on the lunar samples suggest that major chemical fractionation occurred at 4.4 Ga. It is inferred from both whole-rock Rb-Sr isochron and Nd-Sm systematics. It is stressed that any models on the lunar petrogenesis and evolution should reconcile with this early fractionation. A model for chemical evolution of the Moon (extensive fractional crystallization of a molten layer, followed by impact melting and mixing of melts) is discussed to account for phase relations and r.e.e. abundances. Similar chronological characteristics are observed for achondrite parent body. Achondrite parent body experienced a similar evolutionary history to the Moon starting with a slightly different initial composition (major elements). In the Earth, on the contrary, chemical differentiation has continued (or is still continuing) as indicated by chronological and isotopic evidence.

INTRODUCTION

The lunar samples have provided an opportunity not only to work on themselves but also to discuss possibilities on the evolutionary history of the Earth and meteorites as well as the Moon. The comparative studies of these planetary objects would, no doubt, lead to a better understanding of the evolution of the solar system. In this article, we focus our attention to chronological and chemical aspects of the lunar studies in connection with the chronology and chemistry of the achondrites and the Earth. A model for the chemical evolution of the Moon is discussed based on the major element compositions, phase relations and abundances and distributions of rare earth elements (r.e.e.). A comparison is made among the planetary objects with respect to their chemical evolution and possible primary composition for rare earth elements.

CHRONOLOGY OF THE MOON‡

The Rb-Sr internal isochrons (mineral isochrons) have been obtained for many mare basalts since Apollo 11 mission returned lunar samples. It appears that each landing site has a characteristic age (allowing some scatter). ^{39}Ar-^{40}Ar method has given ages consistent with Rb-Sr mineral isochron ages. The discrepancy in the ages between Rb-Sr and U-Pb methods could be minimized by a new plot proposed by Tera *et al.* (1972), so that it may be concluded that these methods give ages with a reasonable agreement. The characteristic ages for each of the landing sites are: Apollo 11 = 3.7–3.8 Ga; Apollo 12 = 3.25; Luna 16 = 3.4; Apollo 15 = 3.25–3.45; Apollo 17 = 3.7–3.8. These ages are generally interpreted to represent the

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† Associée au CNRS no. 196.

‡ References are too many to refer to. For details, refer to the paper by Wasserburg, this volume, p. 7.

igneous events (i.e. formation of mare basalts). However, the fact that most of Rb and thus radiogenic ^{87}Sr in the mare basalts are concentrated in the minor phase(s) very rich in K led Birck *et al.* (1975) to raise a question that a mineral isochron may be a mixing line among the 'high-K phase' and the major phases such as plagioclase and pyroxene. The ages obtained by Nd-Sm method (Lugmair *et al.* 1975) agree with those of Rb-Sr, which strongly suggests that the isochron ages represent the time of mare basalt formation for each landing site.

In contrast to the mare basalts, the highland breccias (anorthositic and noritic breccias) have ages 3.9–4.0 Ga (by both Rb-Sr and ^{39}Ar-^{40}Ar methods). These ages are generally interpreted as metamorphic resetting ages because the texture and mineralogy of the highland breccias indicate shock and metamorphism. Evidence for isotopic disequilibrium among minerals has been found by Papanastassiou *et al.* (1973). Tera *et al.* (1974) suggested that the reason why the highland rocks show a rather narrow range of ages would be that a cataclastic event occurred at 3.9–4.0 Ga which erased almost all earlier records with respect to parent–daughter systems. They suggested that the cataclystic event to be very extensive meteoritic impacts, which is not inconsistent with the orbital calculations of meteorites given by Wetherill (1975). Nevertheless, the records of the events earlier than 4.0 Ga have been found in the ages of dunite 72417 (4.6 ± 0.1 Ga) and troctolite (4.5 ± 0.1 Ga) (Papanastassiou *et al.* 1975 and suggested also by Schaeffer *et al.* (1975) and Turner & Cadogan (1975) on the basis of ^{39}Ar-^{40}Ar technique).

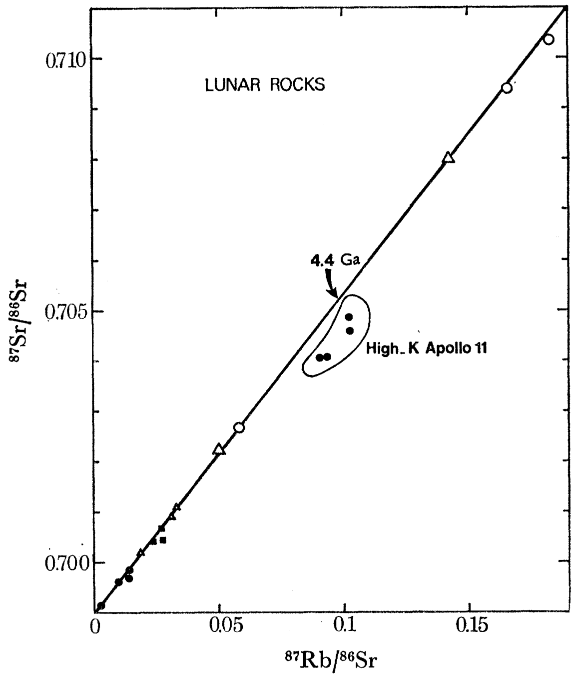


Figure 1. Whole-rock Rb-Sr isochron of the lunar igneous rocks. ●, Apollo 11; ○, Apollo 14; ■, Apollo 15; △, Apollo 12.

In addition to the ages of 'events' given above, an important information of the lunar history is given by a whole-rock isochron plot. As shown in figure 1, whole-rock samples of basalts define an isochron of 4.4 Ga (except for high-K Apollo 11 basalts which show a younger model age). Birck & Allègre (1972, 1975) demonstrated that whole-rock samples of the highland breccias also define an isochron of 4.4 ± 0.1 Ga (figure 2). We interpret the age to represent the time of the major chemical fractionation probably occurred in the entire Moon because the age is common to the maria and the highland.

Tera *et al.* (1974), on the basis of U-Pb systematics, suggested an early chemical fractionation at 4.4 Ga, and Lugmair *et al.* (1975) showed that the Nd-Sm systematics of the source area of a lunar basalt had been established at 4.4 Ga. Thus, Rb-Sr, U-Pb and Nd-Sm relationships suggest that a major chemical fractionation of the whole moon occurred at 4.4 Ga. It is important to note that there is no younger internal igneous activity dated on the Moon.

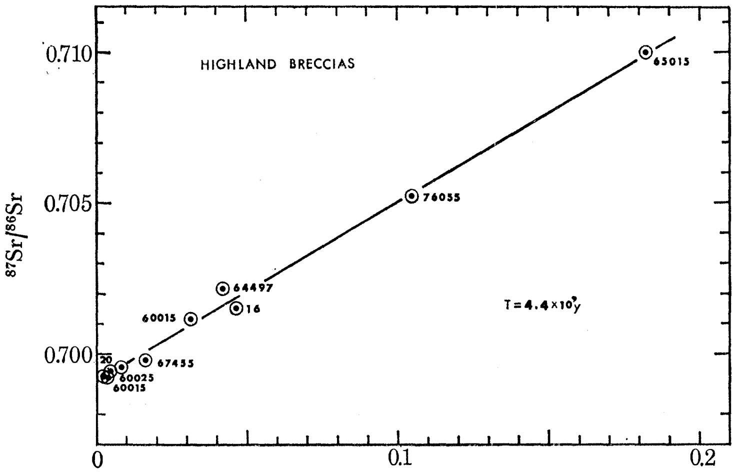


FIGURE 2. Whole-rock Rb-Sr isochron for the lunar highland breccias. Birck *et al.* (1972, 1975, in preparation).

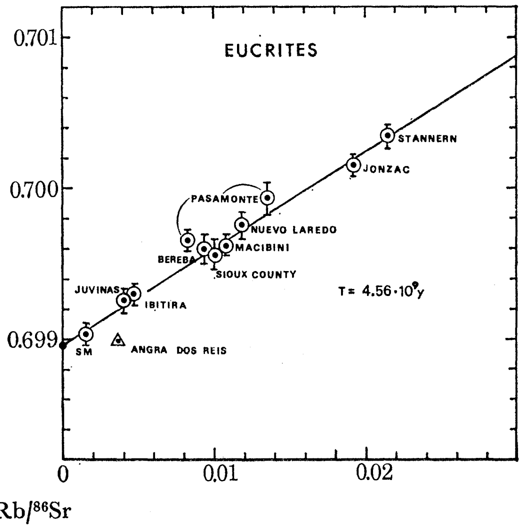


FIGURE 3. Whole-rock Rb-Sr isochron for eucrites. Allègre *et al.* (1975), Birck *et al.* (1975).

CHRONOLOGY OF THE ACHONDRITE PARENT BODY (a.p.)

As will be discussed later, some of the silicate-rich achondrites (diogenites, howardites and eucrites) appear to be cogenetic, representing various stages of a magmatic differentiation sequence, we interpret the chronological data on achondrites in a similar way to that for the lunar chronology. The recent determinations of the Rb-Sr internal isochrons of eucrites (Allègre *et al.* 1975; Birck & Allègre 1975) are summarized as follows: (1) The eucrites Juvinas and Ibitira give an age of 4.56 Ga. The non-brecciated structure of Ibitira suggests that this age would be of fundamental importance. The Nd-Sm mineral isochron obtained for Juvinas (Lugmair 1974) gave an age of 4.56, being in absolute agreement with Rb-Sr results. (2) An age of 4.2 Ga, well defined for Bereba and Sioux County eucrites would probably represent either a later igneous event or a metamorphic resetting. (3) Eucrites Stannern and Pasamonte show highly disturbed Rb-Sr systematics, as experimental points do not define a line. The maximum age calculated for a high-K phase is 3.2 Ga for Stannern and 2.6 Ga for Pasamonte. Papanastassiou *et al.* (1974) also obtained a mineral isochron age of 3.6–3.8 Ga for the howardite Kapoeta and Papanastassiou & Wasserburg (1974) reported an age of 1.3 Ga for the nakhlite Nakhla.

Similar to the whole-rock lunar samples, the whole-rock eucrites define a Rb-Sr isochron of 4.56 Ga (figure 3). The same age has been obtained by U-Pb method on some of the eucrites

(Tatsumoto *et al.* 1973; Manhes *et al.* 1975), although some of shem show significant discordancy when plotted on a concordia diagram.

It has been well demonstrated that ^{244}Pu-derived fissiogenic Xe are present in eucrites and howardites (e.g. Reynolds 1968). If correlation between U content and Xe anomaly, which suggests the *in situ* decay, were true, the fact may be taken to indicate that these meteorites are old objects, and therefore the young ages observed by Rb-Sr should be interpreted as metamorphic resetting (probably related to impact metamorphism) ages. By analogy with the Moon, it may be suggested that the achondrite parent body (a.p.) experienced the major chemical fractionation at 4.56 Ga (defined by whole-rock isochron). Similarly to the Moon, there seems to be no younger internal igneous activity of the a.p.

Chronology of the Earth

The chronological results on the terrestrial rocks relevant to the discussion in this paper include those on the 'oldest' rock of the Earth. Since the pioneer work on Greenland by Oxford Group (Black *et al.* 1971), many old rocks have been reported. To the best of our knowledge, the oldest rocks dated are those of the Goothaab area (Greenland) which have an age of 3.7 Ga (Black *et al.* 1971). The Montevideo gneiss of the Minnesota Valley gives 3.4 Ga (Fahrat & Wetherill 1975: cf. 3.9 Ga reported by Goldich *et al.* 1975). These ages have been confirmed by our recent measurements with the single-zircon technique (Lancelot & Allègre 1975). The basement complex in Rhodesia seems to have rocks as old as 3.6 Ga (Hawkesworth *et al.* 1975) and ages ranging from 3 to 3.3 Ga have been reported for some areas including South Africa, Sahara and Australia. Total surface area of these rocks appears very limited but it is conceivable that most of the old record has been erased by later events. It should be noted that these 'oldest' rocks are younger than most of the lunar and achondritic samples. Considering the common age for the Earth, the Moon and the a.p., the apparently 'younger' ages for the terrestrial rocks require an explanation. A possibility would be the effect of meteorite impact (i.e. the impact events effectively erased the older record by melting or strongly metamorphosing the re-existing rocks). The surface pictures of Mercury and Mars taken by Mariner 10 and MVM Mission (McCauley *et al.* 1974 and Murray *et al.* 1974) show an abundance of impact craters on these planets, suggesting that two planets on both sides of the Earth (relative to the heliocentre) were subjected to the impacts. By analogy with the moon (Tera *et al.* 1974), extensive impacts might have occurred around 4.0 Ga and erased the previous igneous/metamorphic events.

A statistical treatment of a volume of the chronological data on the Precambrian terranes indicates that igneous activities synchronous with folding (orogenesis) show 'periodicity'. As shown in figure 4, the statistical maxima are observed at 2.7, 2.4, 2.1, 1.75, 1.45, 1.05, 0.6 Ga. On the contrary, syn-orogenic magmatism in the period younger than 0.6 Ga seems more or less continuous on the world-wide scale (Allègre 1972).

Another point to be mentioned for the Earth is that Sr and Pb isotopic composition of basaltic rocks (e.g. Tatsumoto, 1966*a*, *b*; Gast *et al.* 1964; Bence 1966) suggest that the mantle has been open with respect to parent-daughter systems. Manhes & Allègre (1975) suggested that the Pb isotopic composition for the mantle 2.0 Ga ago estimated from the lafic rocks of the Kola Peninsula could be used to calculate the age of the Earth of 4.58 Ga, based on the closed-system assumption. This, in turn, suggests that if 4.58 Ga is taken, the mantle for the

Kola Peninsula had been closed with respect to U and Pb to 2.0 Ga. Hart & Brooks (1970) and Montigny *et al.* (1969) discussed models of Sr isotopic evolution of the mantle involving continuous change of Rb/Sr ratio. The open system nature of the mantle with respect to Rb-Sr and U-Pb systems suggests that chemical fractionation (at least with respect to these elements) of the mantle continued or is still continuing today. This is in a strong contrast to the Moon and the a.p. for which the major chemical fractionation occurred only in the very early part of the history. The delayed (or continued) chemical fractionation and magmatism appear to be unique characteristics of the Earth compared with the moon and the a.p., which may well be related to the characteristic thermal history of the Earth. If the accretion process for the Moon was rapid as suggested by some authors (Mizutani *et al.* 1972; Hanks & Anderson 1972; Toksöz *et al.* 1972) and if the Moon was formed at the similar distance from the Earth as it is today, the temperature of the Earth would have also been quite high in a very early part of its history (Wetherill 1972). The subsequent cooling could largely depend on the size of the planets in such a way that the larger the body, the more delayed was the cooling and thus chemical fractionation.

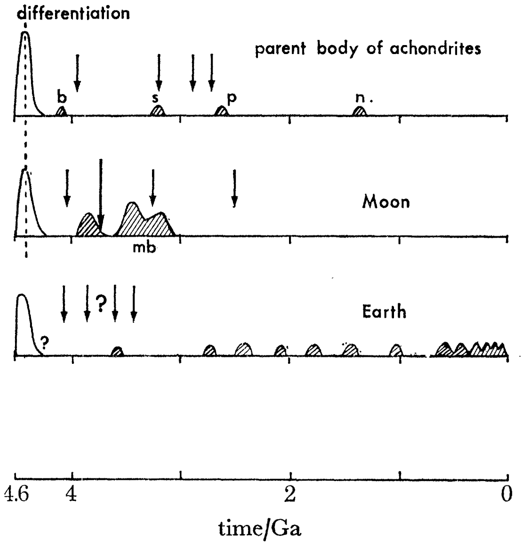


FIGURE 4. Chronological comparison of the Earth, the Moon and a.p. Arrows indicate meteorite mpacts. Hatched areas represent dated events. For a.p.: b, Bereba; s, Stannern; p, Pasamonte; n, Nakhla. For Moon: mb, mare basalts.

CHEMICAL EVOLUTION OF THE MOON

Comparison of the chronological patterns summarized above (see figure 4) shows a contrast between the Earth, and the Moon and the a.p. For the Moon and the a.p., we emphasize the significance of the early chemical fractionation inferred from the whole-rock isochron of 4.4 Ga for the Moon and 4.56 Ga for the a.p. This chemical fractionation must have involved many elements as it is suggested by U-Pb (Tera *et al.* 1974), Rb-Sr (e.g. Allègre *et al.* 1975) and Nd-Sm (Lugmair *et al.* 1975). As pointed out by Birck *et al.* (1972) and Provost *et al.* (1975), this should be taken as a very strong constraint for any evolutionary model for these objects.

We first examine a volume of trace element data on the lunar samples (such as those compiled by Hubbard (personal communication)) in terms of simple fractional crystallization and partial melting models using two-element plots (such as figures 6 and 7). Fractional crystallization could be expressed by the Rayleigh equation:

$$C_l = C_0 F^{D-1}, \tag{1}$$

where C_l denotes concentration of an element in liquid, C_0 the original concentrations, F the fraction of liquid remaining and D the partition coefficient (solid/liquid). If D values are very small (relative to 1), for a pair of elements (U and Th, for example)

$$C_l^1/C_l^2 = C_0^1/C_0^2. \tag{2}$$

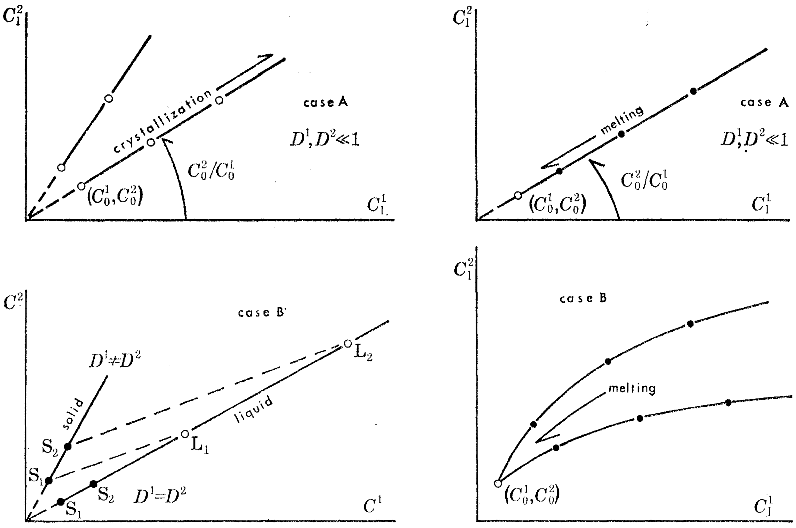
Therefore, if the element 1 is plotted against the element 2, the points should fall on a straight line which passes through the origin and the slope corresponds to the ratio of these elements in the initial liquid. The solid concentration is given by

$$C_s = DC_l = DC_0 F^{D-1} \tag{3}$$

and thus

$$C_s^1/C_s^2 = C_0^1/C_0^2 \times D^1/D^2. \tag{4}$$

Only if $D^1 = D^2$, the solid trend is exactly the same as the liquid trend in the same plot. Even if D^1, $D^2 \leqslant 1$, the solid trend could be quite different from the liquid trend depending on the ratio D^1/D^2. Figure 5 shows the solid and liquid trends in fractional crystallization process.



fractionation

partial melting

Figure 5. Contrasting trends of trace elements produced by fractional crystallization and partial melting. Fractional crystallization: case A, D^1, $D^2 \leqslant 1$, see text. For case B, note different trends for solids (S_1, S_2) and liquid when $D^1 \neq D^2$. Partial melting: case A, D^1, $D^2 \leqslant 1$ and F. Case B, D^2 is significant relative to F. Significant part of element 2 is retained in the solid phase, so that the curved trend is obtained.

In partial melting, we have

$$C_l = C_0/F + (1-F)D, \tag{5}$$

where C_l denotes the concentration of liquid, C_0 the original solid concentration, F the fraction of melt, D the bulk partition coefficient. If D is small (negligible relative to F),

$$C_l = C_0 F^{-1} \tag{6}$$

and hence

$$C_l^1/C_l^2 = C_0^1/C_0^2. \tag{7}$$

Therefore, the trend similar to figure 5 results. However, once either of D^1 or D^2 becomes significant relative to F, (7) does not hold and the resultant trend becomes completely different. Figure 5 illustrates these contrasting trends. The basic concept briefly described here has been developed by Treuil & Varet (1973) and Treuil & Joron (1975) and has been applied to distinguish the contrasting trends resulted from partial melting and fractional crystallization of terrestrial rocks (e.g. Barberi *et al.* 1975).

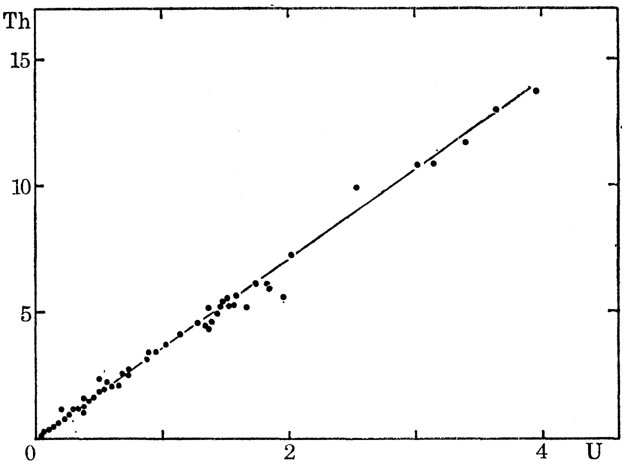


FIGURE 6. Th-U relation of the lunar rocks. Data from compilation of Hubbard (1975).

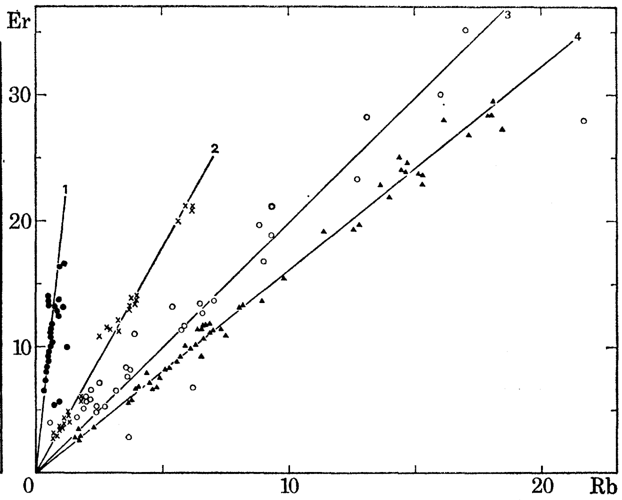


FIGURE 7. Er-Rb relations of the lunar rocks. trend 1: Apollo 12 and 15 mare basalts. trend 2: Apollo 11 and 17 mare basalts. trends 3 and 4: non mare rocks. Kreep plots on trend 4.

In figures 6 and 7, we observe two contrasting situations in the lunar samples, which would easily be understood by the concept described above. Th and U concentrations show a single linear trend (figure 6), while several different trends (note that all trends pass through the origin) are observed for Er and Rb (figure 7). Comparing these figures with figure 5, we interpret that the Th-U trend corresponds to case A of fractional crystallization in figure 5. For Er-Rb, there seem to be several possibilities including (1) four different fractional crystallization trends resulted from four different initial liquids and (2) trends 3 and 4 correspond to those of liquids but 1 and 2 represent the solid trends associated with 3 and 4. Each of these interpretations has quite different implications with regard to the chemical evolution of the Moon, and we will return to the point later. It is important to note here that none of the trends in Er against Rb plot (figure 7) fits with that of the partial melting.

As mentioned earlier, an important implication of the chronological studies is that the Moon (or at least its near-surface part) had experienced major chemical differentiation at 4.4 Ga and subsequent process (i.e. mare basalt formation) could not disturb Rb-Sr and Nd-Sm systems established at 4.4 Ga. It has been suggested that the outer part of the Moon was molten due to the heat generated by rapid accretion (Mizutani *et al.* 1972; Hanks & Anderson 1972; Toksöz *et al.* 1972). The subsequent crystallization process of the molten Moon could then correspond to early chemical fractionation inferred from chronology. During this process, trace element fractionated according to the phase present and the partition relationships of the trace elements among the phases involved. If this process could be approximated by fractional crystallization, the trace element correlations such as those in figures 6 and 7 could be interpreted to illustrate the early chemical fractionation. The range of concentrations of Er and Rb may be too great for a simple solid trend. In this case, minor fractionation is to be considered following the second-stage melting. It is important to note that 'kreep' plots on the trend 4 together with other non-mare rock types. This should be taken as an indication that kreep (or at least kreep components) was formed as residual liquid during fractional crystallization process of 4.5 Ga. A small-degree partial melting has been suggested for kreep origin by many authors simply on the ground that it has high trace element concentrations. However, this model is very difficult to reconcile with the fact that kreep also plots on the 4.4 Ga whole-rock Eb-Sr isochron, if plagioclase is left behind melting. Walker *et al.* (1973), for example, suggested anorthosite-norite-troctolite suite (a.n.t.) as a possible source for kreep. If this were the case, a small-degree partial melt would be in equilibrium with plagioclase. The partition relationships of Rb and Sr suggest that this liquid would most probably have a higher Rb/Sr ratio than the source material. The subsequent growth of ^{87}Sr/^{86}Sr ratio should be such that the kreep is off the whole-rock isochron of 4.4 Ga as measured today (Birck *et al.* 1972). A similar situation holds true for Sm-Nd systematics. Therefore, even if a partial melting model could escape the difficulty for Rb-Sr systematics by invoking either that all plagioclase is entering the melt or that the source is plagioclase-free, the model still has to reconcile with Sm-Nd systematics. In this context, it is important to note that light r.e.e. depletion (as exemplified by high Sm/Nd ratio relative to chondrite) for the source of mare basalts was established in a very early part of the lunar history (Lugmair *et al.* 1975).

Based on these constraints, we present a model for the chemical evolution of the Moon. It consists of fractional crystallization of the molten surface layer of the Moon and subsequent impact melting and mixing (Provost *et al.* 1975). The diversity of chemical composition in the near-surface parts of the moon was established by fractional crystallization and subsequent melting-mixing is considered particularly to explain the origin of the varieties of rock types actually returned and studied. Very extensive (or probably complete) melting due to meteorite impact is proposed to maintain Rb-Sr and Nd-Sm systematics. Mixing of the impact melts simply move points on the whole-rock isochron and does not disturb the systematics.

Based on the arguments given by Walker *et al.* (1973) that the compositions of the lunar feldspathic rocks can be explained by liquidus phase relations at low $P(O_2)$ of the system olivine-anorthite-silica, we made calculations to determine crystallization paths, composition of both solid and liquid, and r.e.e. concentrations in both solid and liquid on various initial compositions and at various stages of fractional crystallization (Provost *et al.* 1975). The results are shown in figure 8. Among a number of different initial compositions (designated after the crystallizing phases, e.g. a.f.e. stands for anorthite-forsterite-enstatite) in the pseudoternary system, two of them, f.a.e.s. and a.f.e.s. provided reasonable results. Furthermore, these two compositions (or compositions in these two zones) appear most plausible for the initial liquid composition of the lunar fractionation. The initial fractional crystallization must be capable of covering the entire range of r.e.e. concentration levels and patterns, since subsequent mixing process tends to reduce the range. Comparing figure 8 with the observed varieties of r.e.e. patterns (figure 9), it may be concluded that a simple fractional crystallization is capable of producing essential features of the lunar r.e.e. patterns. A better approximation to the lunar differentiation could be expected by having diopsidic pyroxene as a fourth component and thus carrying out similar calculations for the system olivine-diopsidic pyroxene-anorthite-silica. Introduction of clinopyroxene seems important to have light r.e.e. depletion in solid which becomes a source of mare basalts. In the figure, only concentrations relative to the initial are shown. Assuming that the initial concentrations are equal to those of chondrite, the figure can be compared directly with conventional chondrite-normalized r.e.e. diagrams.

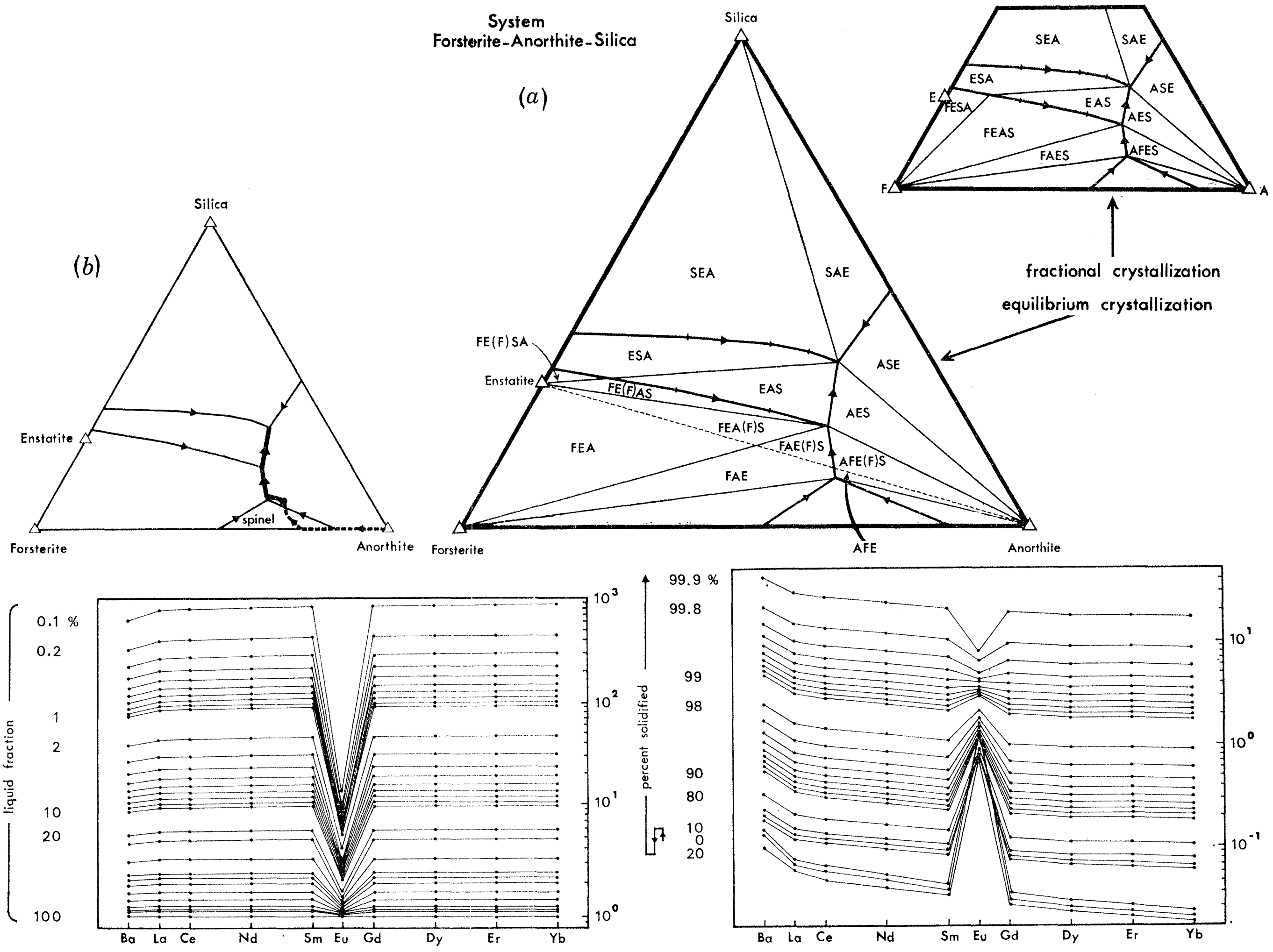


Figure 8. Fractional crystallization model for the Moon (Provost *et al.* 1975). (*a*) Liquidus phase diagram of the system forsterite-anorthite-silica with zones of liquid composition leading to unique crystallization paths. Faes stands, for instance, for forsterite-anorthite-enstatite-silica mineral (phases appear in this order). The real calculations in this paper were made with variable Fe/Fe + Mg ratios. Note that the boundaries in the figure are shifted as a function of Fe/Fe + Mg. (*b*) An example of the results. The initial liquid is in zone afes. Ree patterns for liquid and solid phases at various stages of fractionation.

According to this model, the early differentiation of the moon may be described as follows. Due probably to the heat generated by rapid accretion, near-surface part of the Moon was molten (probably to the depth of several hundred kilometres). Crystallization of the molten layer first produced either dunitic cumulate or anorthositic one depending on the composition. If the composition were indeed close to that of the white inclusion in Allende (Ganapathy & Anders 1974), the first product must be dunite (Hodges & Kushiro 1974). Crystallizing mafic phases sank to the bottom, while anorthite floated, resulting in anorthositic lid on the top and mafic cumulate at the bottom. Thickness of the lid and bottom layer increased as crystallization proceeded. The latest-stage liquid could then have been concentrated just below the anorthositic lid. Later impact events excavated the layered structure to various depths, producing melts of various parts of the layer and mixing them at various proportions. For example, kreep lay have been derived by mixing latest-stage liquid and earlier-stage cumulate. A simple calculation suggests that Mg/Mg + Fe ratio of kreep (0.6) can be modelled by mixing 30 % of the latest-stage material (Mg/Mg + Fe = 0, for an extreme case) and 70 % of early-stage material (Mg/Mg + Fe = 0.9). These proportions then yield r.e.e. pattern of the mixture (overall concentration levels of 300–400 times chondrite and a large negative Eu anomaly) quite smilar to those actually observed for kreep. Similarly, we consider that mixing (or contamination) of different liquids (particularly with one which represents the latest-stage liquid) is important for any other rock types on the moon. Similar contamination hypothesis has been proposed by Tera *et al.* (1970) and Wasserburg *et al.* (1973) to account for trace elements and Sr isotope ratios. Figure 10 summarizes the sequence of events described above.

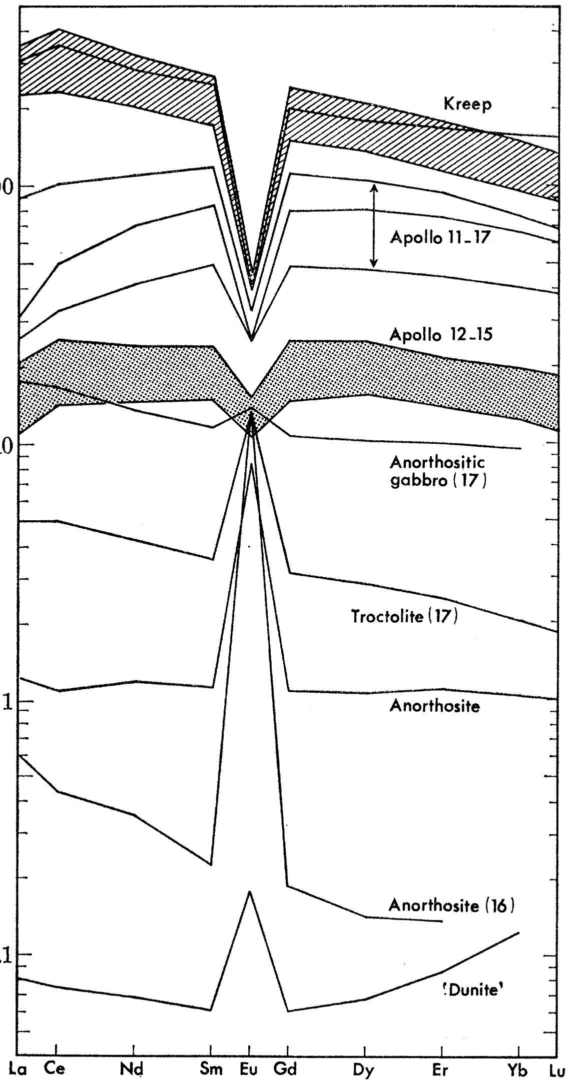


FIGURE 9. Summary of the r.e.e. patterns observed for the lunar samples.

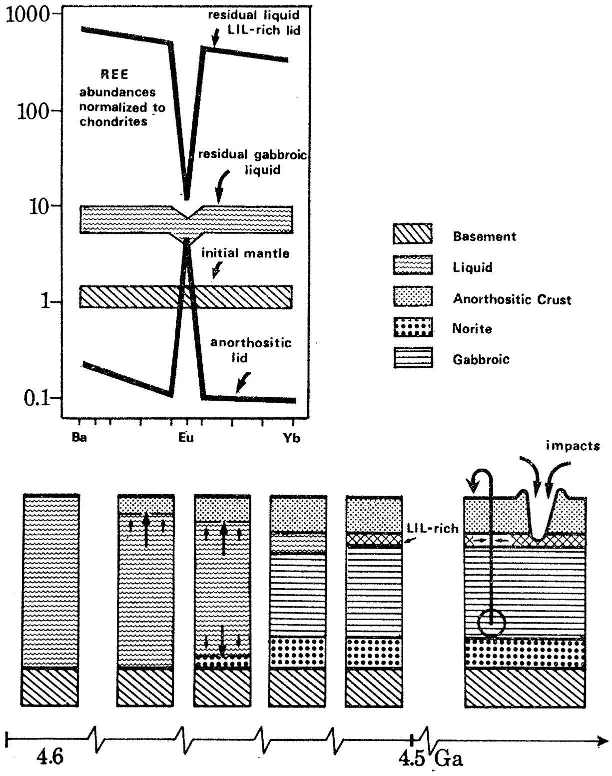


FIGURE 10. Sequence of events (chemical evolution) of the Moon.

The initial composition of the Moon, in terms of both major and trace elements have attracted some attention (e.g. Ganapathy & Anders 1974; Wänke *et al.* 1975). Hodges & Kushiro (1974) determined phase relations at high pressures on a possible moon composition and also suggested that a composition containing more Al_2O_3 than the one they worked on could be more plausible. From a melt of this composition anorthite crystallizes after olivine, so that the order of crystallization is very similar to the one considered in our model. It should be noted that our model based on the chondritic r.e.e. abundances (absolute abundances equal to chondrite) is capable of producing the observed features of the lunar r.e.e. patterns. This, in turn, suggests that the initial concentrations, in terms of r.e.e., may be equal to or a little higher than chondrite.

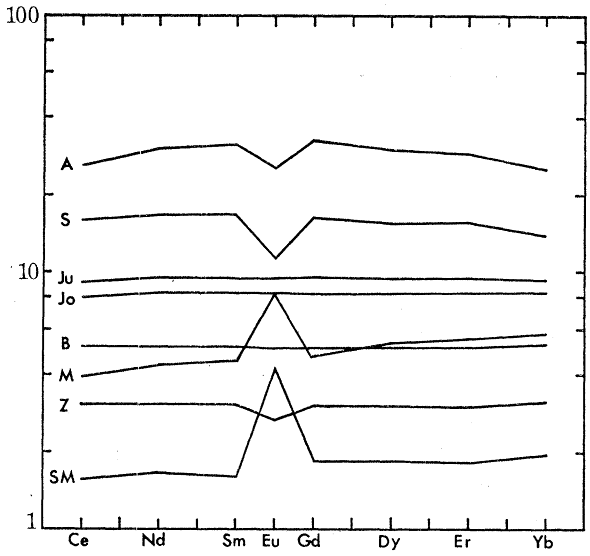


FIGURE 11. Summary of the r.e.e. patterns observed for achondrites. Data from Schnetzler & Philpotts (1969). A, Angra dos Reis (angrite); S, Stannern (eucrite); Ju, Juvinas (eucrite); Jo, Jonzac (eucrite); B, Bununu (howardite); M, Moore County (eucrite); Z, Zmenj (howardite); SM, Serra de Magé (eucrite).

CHEMICAL EVOLUTION OF ACHONDRITE PARENT BODY

A similar approach to the Moon seems reasonable for the achondrite parent body (a.p.), since they show gross similarity in both the chemical compositions and chronological characteristics. The first step should therefore be the discussions on genetic relationship among varieties of achondrites (e.g. diogenites, howardites and eucrites). The examination of the major element composition of achondrites in the light of the liquidus phase relations led Shimizu & Allègre (1975) to suggest a close genetic link among diogenites, howardites and eucrites. They demonstrated that eucrite composition, when projected onto olivine-anorthite-silica and forsterite-fayalite-silica is remarkably close to a cotectic liquid, while howardite composition can be interpreted as solid cumulate in equilibrium with eucritic liquid. They also suggested that the diogenites could represent earlier-stage cumulates crystallized from a pre-cotectic liquid. The relationship could be interpreted further to represent a magmatic differentiation process occurred in the parent body of achondrite at 4.5 Ga ago. Ringwood (1961) among others suggested similar magmatic crystallization sequence including pallasites to represent the earliest stage cumulates. If this were the case, the order of phases in crystallization is olivine, followed by Ca-poor pyroxene (protohypersthene and then pigeonite), plagioclase and Ca-rich pyroxene. This is in contrast with the crystallization sequence estimated for the Moon for which plagioclase joins olivine as the second phase. The difference in the order (and thus the course) of the crystallization between the Moon and a.p. is well illustrated by r.e.e. patterns. Figure 11 summarizes the r.e.e. patterns observed for achondrites (Schnetzler & Philpotts 1969). Comparing with figure 9, the most significant difference seems to be that the lunar samples show much larger Eu anomaly, which is consistent with more significant participation of plagioclase for the lunar differentiation. Another difference is that the differentiation for achondrites appears to be terminated at the peritectic point (olivine-pyroxene-plagioclase), while lunar differentiation probably went further. This difference might be due to near-equilibrium crystallization for a.p. and extreme fractionation for the Moon. The difference in the course of crystallization may be due to a small difference in the initial composition, particularly in terms of plagioclase component (being higher in the Moon than a.p.).

Comments on chemical evolution of the Earth

The chronological and isotopic evidence suggests that chemical history of the Earth is far more complex than the Moon and a.p., and it is clearly beyond the scope of this paper to synthesize chemical evolution of the Earth. A remarkable feature for the Earth (compared with others) is that partial melting is equally important relative to fractional crystallization. This would be one of the reasons for complex isotopic growth (parent–daughter fractionation may be expected during this process). It should also be noted that if one treats trace element data of the terrestrial rocks with the concept described earlier, the trends for both fractional crystallization and partial melting are observed (Treuil, unpublished manuscript). Another consequence of partial melting is that relative fractionation of r.e.e. is much more pronounced in terrestrial rocks than the lunar and achondrite samples in which essentially parallel shift is only observed (figures 9 and 11). This is also due to presence of garnet (by which r.e.e. are effectively fractionated) at relatively shallow depth (about 80 km) in the Earth's mantle compared with around 600 km in the lunar mantle, so that the effect of garnet may be relatively easy to observe on the Earth. The fact has been effectively used by Loubet *et al.* (1975) to estimate the initial r.e.e. concentrations of the earth's mantle. The estimated values (2–2.5 times chondrite) are consistent with the previous estimate such as those of Allègre *et al.* (1973) (1–2 times chondrite) based on the material balance calculations on constituent rock types of ophilites.

These arguments suggest that the r.e.e. concentrations of the Earth, the Moon and a.p. were close to each other and in the range of 1–2.5 times chondrite.

We thank our colleagues J. L. Birck, A. Provost, M. Loubet, G. Manhes and J. F. Minster for discussion.

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