ALKALI ELEMENT CONSTRAINTS ON EARTH-MOON RELATIONS
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Given their range of volatilities, alkali elements are potential tracers of temperature-dependent processes during planetary accretion and formation of the Earth-Moon system. Under the giant impact hypothesis, no direct connection between the composition of the Moon and the Earth is required, and proto-lunar material does not necessarily experience high temperatures [1]. Models calling for multiple collisions with smaller planetesimals derive proto-lunar material mainly from the Earth's mantle and explicitly invoke vaporization, shock melting and volatility-related fractionation [2]. Na/K, K/Rb, and Rb/Cs should all increase in response to thermal volatilization, so theories which derive the Moon substantially from Earth's mantle predict these ratios will be higher in the Moon than in the primitive mantle of the Earth. Despite the overall depletion of volatile elements in the Moon, its Na/K and K/Rb are equal to or less than those of Earth. A new model presented here for the composition of Earth's continental crust, a major repository of alkali elements, suggests the Rb/Cs of the Moon is also less than that of Earth. Fractionation of the alkali elements between Earth and Moon are in the opposite sense to predictions based on the relative volatilities of these elements, if the Moon formed by high-T processing of Earth's mantle. Earth, rather than the Moon, appears to carry a signature of volatility-related fractionation in the alkali elements. This may reflect an early episode of intense heating on Earth with the Moon's alkali budget accreting from cooler material.

Moon: Rb/Cs ratios of lunar rocks typically fall between 10 and 40 with mare basalts and KREEP defining a value of about 22 ± 3 [3,4]. There may be resolvable differences in the compositions of pyroclastic glasses compared to crystalline mare basalts, with pyroclastic glasses having lower Rb/Cs ratios, closer to chondritic and more similar to those of pristine lunar highlands rocks. A composite sample of Apollo 15 green glass had a Rb/Cs of about 15 [5], and individual spherules of Apollo 17 orange glass have remarkably low Rb/Cs ratios of 6-18, averaging 10 [6]. This average value is notably similar to that of CI chondrites (Rb/Cs = 12; [7]). However the database remains exceedingly small as only 5 of the spherules analyzed by [6] gave both Rb and Cs data.

Estimates of the bulk composition of the lunar crust are somewhat variable, with [9] deriving values of 1.7 ppm Rb and Rb/Cs = 24, essentially that of KREEP, compared to 0.7 ppm Rb and Rb/Cs = 35 from KREEP-free lunar meteorites [10]. It is not clear what the high Rb/Cs component is in the lunar meteorites, as pristine lunar highlands rocks tend to have Rb/Cs ratios somewhat lower than that of KREEP, typically 2-20, averaging around 15 [3,4]. The low Rb and Cs concentrations in pristine ferroan anorthosites make them an inconsequential geochemical reservoir, but Mg-suite norites have Rb contents of around 1-5 ppm and could contribute significantly to the overall bulk composition of the lunar crust [8].

The Moon probably has a Rb/Cs of between 15-25, similar to the meteoritic values of 16-24 for eucrites and howardites, and 14-17 for shergottites [11]. Portions of the Moon may have Rb/Cs ratios close to the chondritic value although these volatile-enriched reservoirs cannot be of volumetric significance. The Rb/Cs ratio of the Moon is not unique in the solar system, and an additional stage of high-temperature processing beyond the general volatile depletion observed for the eucrite parent body is not apparent in the alkali element signature of the Moon.

Earth The depleted mantle of the Earth has a Rb/Cs of 85 ± 20, as shown by fresh tholeiitic basalts from mid-ocean ridges and ocean islands [12]. Direct determination of the alkali content of the mantle via ultramafic xenoliths is difficult because of their low concentrations of alkali elements, particularly Cs, and the potentially severe effects of weathering, alteration and metasomatism, all of which tend to lower Rb/Cs ratios of xenoliths [13]. The 'most primitive' San Carlos xenolith of [14] has a Rb/Cs of 103, similar to that of fresh oceanic tholeites. Least-metasomatized mantle xenoliths from SE Australia also have Rb/Cs values of about 100 [13].

High concentrations of alkali elements in the continental crust make it a significant repository of these elements [4]. However, alkali element compositions of the bulk continental crust are
ALKALI ELEMENTS IN THE EARTH AND MOON  Norman M.D., Drake M.J. and Jones J.H.

poorly known due to the highly mobile nature of these elements during weathering and metamorphism. A Rb/Cs value of 19 ± 11 for the upper crust has been derived from sediments, sedimentary rocks, and loess [4], leading to bulk continental and primitive mantle values of 25 and 28, respectively. This bulk earth value would indicate similar compositions for the Earth and Moon. The mass balance model offered by [4] could not account for the Earth's budget of Rb and Cs from the continental crust, oceanic basalt reservoir (MORB+OIB), and oceans, and invoked a hypothetical less-depleted mantle reservoir. An alternative mass balance model by [15] that relied solely on known geochemical reservoirs determined a primitive mantle Rb/Cs of around 40, indicating a significant compositional difference between Earth and Moon.

Although sediments are especially suitable for estimating upper crustal abundances of insoluble elements (REE, Th, Sc) [16], this approach may not be appropriate for the alkalies due to the unequal selectivity of clay minerals (Cs>Rb>K>Na) [17], their orders of magnitude longer aqueous residence times compared to the REE [16], and the rapid (<1 m.y.) fractionation of these elements during subaerial weathering [18]. Alternatively, primary crystalline rocks may provide more direct constraints on the composition of continents. Despite intensive investigations of alkaline element concentrations in crustal rocks, the dataset for rocks which may be considered primary continental material is surprisingly sparse. Archean felsic rocks which have K/U ratios close to the nominal crustal and bulk Earth value (10,000) have Rb/Cs ratios averaging 35 [19]. The K/U ratio of these rocks suggests their mobile elements may not have been severely modified. Coexisting sediments are consistent with this composition, but range to lower Rb/Cs and K/U [20]. Granulites typically have higher Rb/Cs and K/U [4, 19].

Phanerozoic I-type granitic batholiths and felsic eruptives provide important samples of younger primary additions to the continental crust. In the western U.S., the temporal progression from Cretaceous sodic batholiths to Tertiary potassic rhyolites is analogous to the classic pattern of crustal evolution in many Precambrian terranes, but without the complication of granulite facies metamorphism. A good example of this analogue within a coherent crustal block is the magmatic evolution recorded by the Idaho batholith and the Snake River Plain (SRP). Idaho batholith tonalites are compositionally similar to Archean sodic tonalites. SRP rhyolites are more potassic and have many geochemical characteristics in common with post-Archean upper crust (REE pattern, La/Th, K/Rb) [21]. Idaho batholith tonalites have Rb/Cs = 44-84, averaging 45, whereas least-fractionated SRP rhyolites have Rb/Cs of 55 [21 and unpub data]. In contrast, tuffaceous sediments from the SRP have Rb/Cs = 17, suggesting significant fractionation of the alkalies during transport and sedimentation. A model for the felsic component of the continental crust based on 75% Idaho batholith tonalite (Archean analogue) and 25% SRP rhyolite (post-Archean analogue; proportions from [16]) has Rb/Cs = 50, K/Rb = 280, Th/U = 3.8 and K/U = 7530.

This model crust produces primitive mantle compositions with Rb/Cs ≥ 40. This value is significantly different from that of the Moon, and in the opposite sense to that expected if the Moon formed by thermal processing of material derived from Earth's mantle. Earth, rather than the Moon, appears to carry a signature of volatility-related fractionation in the alkali elements, possibly reflecting an early episode of intense accretionary heating. The material which accreted alkaline elements to the Moon may have largely escaped similar heating.