Helium Isotopic Evidence for a Lower Mantle Component in Depleted Archean Komatiite

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Archean magnesium-rich komatiites require hot and presumably deep mantle sources, but their trace-element composition and radiogenic isotope composition are similar to those of modern mid-ocean ridge basalts, which originate in the upper mantle. The isotopic composition of helium extracted by sequential crushing of fresh olivines separated from two Archean and one mid-Proterozoic komatiites varies over three orders of magnitude, between a radiogenic end-member rich in helium-4 and a component rich in helium-3. Such helium-3 enrichment suggests the presence of a lower mantle component in Archean komatiites.

Hot material from deep in the mantle rises in plumes and contributes to the generation of oceanic island basalts (OIBs) (*1*). The source of the OIB magmas is chemically and isotopically distinct from the upper mantle source of mid-ocean ridge basalts (MORBs) and may represent a mixture of components from different regions of the mantle (*2*). Komatiites are ultramafic volcanic rocks that erupted at very high temperatures (up to 1600°C) (*3*). They are restricted to the Archean and Proterozoic greenstone belts with the exception of one Cretaceous occurrence in Colombia (*4*). Their petrology has been attributed to melting at great depths (≥400 km) in the centers of hot mantle plumes (*5*). Although there is some evidence from trace-element ratios measured in glass inclusions in komatiitic olivines to relate komatiites to plume-type magmas (*6*), this evidence seemed at odds with the generally depleted trace-element and isotopic character of komatiites (*3*). We present here He isotopic data for Archean and Proterozoic komatiites to refine models for their origin.

The isotopic composition of He has been used to trace the origin of mantle-derived magmas. The two isotopes of He have different origins. Primordial ^{3}He was trapped during Earth's formation and has not been significantly produced in the mantle since then. Mantle ^{4}He results from mixing between a trapped primordial component and a radiogenic ^{4}He produced by the radioactive decay of U and Th throughout geological history. Both He isotopes are degassed from the mantle through magmatism, and the ^{3}He/^{4}He ratios in the different regions of Earth are a function of ^{3}He/(U + Th) ratios and of the residence times of He, U, and Th. High ^{3}He/^{4}He ratios often found in OIBs (up to 32 R_a, where R_a is the atmospheric ^{3}He/^{4}He ratio of 1.386×10^{-6}) indicate a deep mantle component rich in primitive ^{3}He (*7*), whereas lower uniform ^{3}He/^{4}He ratios of MORBs (8 ± 1 R_a) are thought to represent a more degassed and homogenized upper mantle. The isotopic composition of He in Archean and Proterozoic komatiites is unknown, mainly because of the lack of unaltered samples. Fresh olivine crystals, able to store He for long periods (*8*), have been identified in some komatiites. We selected olivines within komatiites from the Ottawa Islands in the Circum-Superior belt of northern Quebec (1.9×10^9 years old) (*9*), from Alexo in the Abitibi belt of Ontario (2.7×10^9 years old) (*10*), and from the Zvishevane region in the Belingwe greenstone belt of Zimbabwe (2.7×10^9 years old) (*11*).

Measurements of He isotopes in these samples (*12*) show that ^{3}He/^{4}He ratios vary over four orders of magnitude (Table 1). Low ratios in the Zvishevane olivines (0.046 ± 0.020 R_a) and in the Ottawa Island olivines (0.12 to 0.18 R_a) indicate radiogenic He produced after lava eruption (*13*) or incorporated through crustal assimilation (*14*). On the contrary, ^{3}He/^{4}He ratios close to 40 R_a found in the first crushing fraction of the Alexo olivines represent the highest value recorded so far in terrestrial lavas (*7*). We have quantitatively evaluated three processes in an effort to understand the high ^{3}He abundance in Alexo olivines: (i) in situ radiogenic and nucleogenic production, (ii) in situ cosmogenic production of ^{3}He during surface exposure of the lava, and (iii) trapping of a ^{3}He-rich mantle component.

The total amount of ^{3}He extracted from the Alexo olivines is two orders of magnitude larger than that produced by natural radioactivity (*15*). In addition, the Zvishevane sample shows radiogenic ^{3}He/^{4}He ratios even though its bulk chemical composition and its age are comparable to that of the Alexo komatiite. For these reasons, it appears unlikely that radioactivity could be

Table 1. Helium isotopic ratios and He and Ne abundances in olivines from komatiites measured in stepwise crushing experiments. Values for He and Ne are corrected from procedural blanks. Ratios of He/Ne much higher than the air value indicate that atmospheric contamination did not significantly affect the He isotopic ratios. n.a., not analyzed; n.d., not detected. The powder remaining after the crushing of sample M712 3 was melted at 2000°C in a resistor furnace (^{4}He blank: 1×10^{-14} mol).

Sample	Number of strokes	He (10^{-12} mol/g)	^{3}He/^{4}He (R_a)	(He/Ne)/(He/Ne)$_{air}$
		Alexo		
M712 1	500	1.88	26.2 ± 0.4	145
	500	0.21	1.7 ± 0.3	n.d.
M712 2	3	0.49	37.2 ± 1.8	n.a.
	10	0.23	22.8 ± 1.4	
	100	8.9	5.9 ± 0.37	
	200	0.27	12.9 ± 1.6	
M712 3	10	0.54	39.1 ± 0.6	n.a.
	100	2.15	8.1 ± 0.3	
	750	19	0.40 ± 0.03	
	10	1.23	0.09 ± 0.04	
	Powder melted	<1.9	<2.3	
		Ottawa Islands		
G18	500	57.5	0.12 ± 0.05	3,064
G21 1	500	27.4	0.17 ± 0.08	10,852
G21 2	10	9.78	0.14 ± 0.06	n.a.
	100	10.6	0.14 ± 0.06	
	500	6.32	0.13 ± 0.06	
	1000	3.62	0.18 ± 0.08	
		Zvishevane		
Z11	500	2.77	0.046 ± 0.020	n.d.

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responsible for the high ^{3}He abundance in Alexo.

Cosmogenic production of ^{3}He results mainly from two processes (*16*). At the surface, fast neutrons constitute the dominant source of ^{3}He and would produce the observed amount of ^{3}He in about 0.4×10^6 years at sea level. Fast muons, which penetrate much deeper and become the dominant source of ^{3}He at a lava depth of 2.6 m (*16*), could produce the observed ^{3}He excess in about 70×10^6 years at this depth. Despite these relatively short durations, we believe that cosmogenic production is not the process responsible for the high ^{3}He/^{4}He ratios in Alexo. First, the high ^{3}He/^{4}He ratios were observed in the first crushing steps of the olivines (Fig. 1), which suggests that ^{3}He-rich He is trapped in fluid-melt inclusions in olivines, such as the ones observed microscopically (*12*). This is at odds with the observation that cosmogenic He is strongly bound to the crystalline lattice of olivine. Indeed, exposure age dating using cosmogenic ^{3}He necessitates that magmatic He be removed in the crushing of olivine grains before cosmogenic He can be recovered by the melting of the remaining olivine powder (*17*). Second, this komatiitic flow was erupted subaqueously, probably in deep water (*10*). Sample M712 comes from the lower cumulate zone and was shielded by ~10 m of lava immediately after emplacement and subsequently by a lava pile >5 km thick. These rocks became part of an orogenic belt, and the sampled outcrop was exposed only after deep erosion and the retreat of continental glaciers about 9000 years ago (*18*). Since then, cosmic rays could have produced only 2.2% of the total ^{3}He.

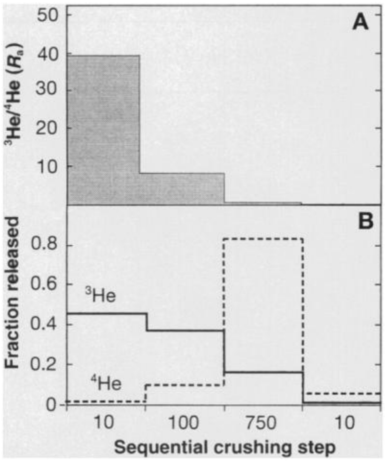

Fig. 1. Abundance and isotopic ratio of He extracted by the sequential crushing of sample M712 3, Alexo komatiite. The ^{3}He/^{4}He ratios (**A**) and the fractions of ^{3}He and ^{4}He released during the successive crushing steps (**B**) are given as a function of the number of crushing strokes.

The Alexo data therefore suggest that these olivines have trapped a mantle fluid with a high ^{3}He/^{4}He ratio. This hypothesis imposes several important constraints on the origin of komatiites and, more generally, on the state of the Archean mantle. This high ratio suggests that komatiites are derived from plumes containing a component from a deep-seated source (*19*). This idea must be reconciled with published trace-element and Nd isotope data, which show that at least part of the plume source of Archean komatiites was geochemically and isotopically depleted, unlike that of the dominant component of most modern OIBs, but similar to that of certain picrites and the Cretaceous Gorgona komatiites (*20*). In fact, the enrichment in present-day OIBs can be attributed to a contribution of recycled material to the source of OIBs and preferential tapping of this material during low-degree melting (*2*). We suggest that, during the formation of komatiites, temperatures were high enough to cause extensive melting of a dominant, refractory, chemically and isotopically depleted component of the plume. The incorporation of ^{3}He-rich deep-mantle material into these variably enriched or depleted mantle components could be responsible for the high ^{3}He/^{4}He ratios (*19*).

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12. Olivine phenocrysts were separated from the cumulate sections of komatiite flows from the Ottawa Islands (samples G18 and G21), Alexo (sample M712), and the porphyritic section of a Zvishevane flow (sample Z11). Large fluid inclusions (20 to 40 μm) have been observed only in Alexo olivines. We were careful to select olivine fragments completely devoid of alteration or macroscopic defects. We did this by selecting 0.3 to 0.5-mm crystal-clear olivine fragments under the microscope. After ultrasonic washing in distilled water and high-grade acetone, the olivine fractions (20 to 100 mg) were loaded in crushing tubes and baked overnight at 150°C. We crushed the samples in several steps by increasing sequentially the number of strokes (Table 1). After purification, all rare gases but He were adsorbed on a stainless steel mesh held at 25 K. We analyzed He with a VG5400 (Fisons Instruments) rare-gas mass spectrometer calibrated with atmospheric He (9.36×10^{-12} mol) and a secondary standard enriched in ^{3}He (hot spring gas from Réunion Island, 1.77×10^{-12} mol, ^{3}He/^{4}He = $12.41 \pm 0.09\ R_a$). The ^{4}He signal was measured on a Faraday collector, and the ^{3}He signal was measured by ion counting. We determined the blanks by crushing olivine phenocrysts for which earlier analyses showed the absence of trapped He [1.3×10^{-15} mol of ^{4}He with ^{3}He/^{4}He = $1.40 \pm 0.35\ R_a$ for 3 strokes (1500 atoms of ^{3}He), and 2.4×10^{-15} mol of ^{4}He for 500 strokes with a similar isotopic ratio]. After He isotopic analysis, Ne was desorbed at 45 K and its amount analyzed (Table 1). The ^{20}Ne blank was 8.2×10^{-15} mol.
13. Helium-4 is directly produced as a result of α-decay of U and Th. This process also produces thermal neutrons responsible for the production of nucleogenic ^{3}He through irradiation of Li atoms. We computed a radiogenic ^{3}He/^{4}He ratio of 0.0017 R_a from the chemical composition of komatiites, using equations developed by J. N. Andrews, *Chem. Geol.* **49**, 339 (1985).
14. Komatiitic lavas can assimilate crustal rocks as a result of thermal erosion during magma ascent and lava eruption, a process that adds crustal He enriched in radiogenic ^{4}He and that could explain the low ^{3}He/^{4}He ratio measured in the Zvishevane and the Ottawa Island komatiites. The Zvishevane sequence overlies continental crust $>3.0 \times 10^9$ years old, and assimilation of this crust is reflected in radiogenic Pb isotope compositions [B. Dupré and N. T. Arndt, *Chem. Geol.* **85**, 35 (1990); C. Chauvel, B. Dupré, N. T. Arndt, in *The Geology of the Belingwe Greenstone Belt, Zimbabwe*, M. J. Bickle and E. G. Nisbet, Eds. (Balkema, Rotterdam, 1993), pp. 167–174]. This would suggest that He, like Pb, is a more sensitive indicator of crustal contamination than the more compatible Nd. In the Ottawa Island komatiite, the case for contamination is very sound. Evidence is found not only in the trace-element ratios and Nd and Pb isotopic compositions but also as a result of an examination of thin sections, which reveals arrays of micrometer-sized fluid inclusions that are likely to be secondary and may represent remnants of secondary fluid circulation.
15. Neutrons produced in a rock have a long path (~10 cm), which largely exceeds the size of the minerals. Therefore, to evaluate the nucleogenic ^{3}He production in olivine (which is devoid of U and Th owing to their incompatibility with this phase), whole-rock U and Th should be used as a source of neutron flux. We estimated the U content to be 18 parts per billion (ppb) from ion probe analysis of the K content in a melt inclusion of olivine [226 parts per million (ppm)], assuming a K/U mantle ratio of 12,700 [K. P. Jochum, A. W. Hofmann, E. Ito, H. M. Seufert, W. M. White, *Nature* **306**, 431 (1983)]. This U content agrees well with that of depleted magmas such as

MORBs. We calculated the maximum amount of Li-produced ^{3}He in the olivine during 2.7×10^9 years from the ion probe analysis of the Li contents of olivines (mean of 1.08 ppm) and of glass inclusions (0.48 ppm). This gives 0.5×10^{-18} to 1.2×10^{-18} mol per gram of ^{3}He as a maximum because complete retention of ^{3}He is assumed. Therefore only 0.7 to 1.7% of the total amount of ^{3}He extracted from the Alexo olivines (Table 1) could have been produced by radioactivity.

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19. One can compute ^{3}He/^{4}He mantle ratios in the past by assuming that they evolved after dilution of solar He (310 R_a) by radiogenic He. For the upper mantle (^{3}He/^{4}He = 8 R_a at present), the maximum He isotopic ratio at 2.7×10^9 years before the present is 16 R_a if the upper mantle remained closed (except for He degassing). Rare-gas characteristics of the mantle can be accounted for by postulating that the upper mantle is in a steady state for these elements, with continuous supply from the lower mantle and release into the atmosphere [L. H. Kellogg and G. J. Wasserburg, *Earth Planet. Sci. Lett.* **99**, 276 (1990); R. K. O'Nions and I. N. Tolstikhin, *ibid.* **124**, 131 (1994)]. This process must be able to preserve the He isotope difference between the upper and the lower regions of the mantle, with the implication that the ^{3}He/^{4}He ratio of the upper mantle should not have varied drastically in the past. We conclude that the Alexo ^{3}He/^{4}He of 40 R_a cannot be characteristic of the upper mantle.
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Transition Element–Like Chemistry for Potassium Under Pressure

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At high pressure the alkali metals potassium, rubidium, and cesium transform to metals that have a d^1 electron configuration, becoming transition metal–like. As a result, compounds were shown to form between potassium and the transition metal nickel. These results demonstrate that the chemical behavior of the alkali metals under pressure is very different from that under ambient conditions, where alkali metals and transition metals do not react because of large differences in size and electronic structure. They also have significant implications for the hypothesis that potassium is incorporated into Earth's core.

Chemical reactivity can be profoundly altered under pressure because large changes can be induced in the chemical bonding, size, and Gibbs free energy of an element (*1, 2*). Compression of the heavy alkali metals K, Rb, and Cs gradually induces a transition from an ns^1 electron configuration to an $(n - 1)d^1$ electron configuration (*1, 3–5*). At pressures above this *s*-to-*d* transition, the alkali metals become transition metal–like elements (*6*).

Although considerable attention has been focused on the changes in the physical properties of the alkali metals that occur under pressure (*1, 3, 4, 7–9*), the effect of the *s*-to-*d* transition on the formation of chemical compounds has not yet been explored experimentally. Various theoretical investigations have reported different results for the effect of pressure on this chemistry (*10*). We now report that, at pressures above 30 GPa, where the *d*-electron character of K is greatly enhanced (*1*), compounds form between K and the transition metal Ni. Thus, the chemical behavior of the alkali metals under pressure is very different from that under ambient conditions (reaction of alkali metals with transition metals under ambient conditions does not occur because of large differences in size and electronic structure). Alkali elements are abundant within Earth's crust, but current knowledge of their chemistry at ambient pressure is probably not applicable beyond moderate depths. These results also suggest that at higher pressures compounds should form in the K-Fe system; this suggestion has important implications for the hypothesis that K is incorporated into Earth's Fe (or Fe-Ni alloy) core (*10, 11*).

The effect of pressure on reactions between alkali metals and transition metals can be estimated by simple rules for alloy formation (*12*) that accurately predict whether a transition metal will form compounds with another metal. According to Miedema's rules, small differences in charge density (ρ_M) at the Wigner-Seitz radius and large differences in work function (ϕ^*) (or electronegativity, which scales with the work function) between two metals favor compound formation (*12*). The electronegativities of the alkali metals and the transition metals with more than half-filled *d*-shells are quite different. However, because the charge densities of the alkali metals are much smaller than the charge densities of the transition elements, the differences in charge density between them are too large to permit compound formation. The only transition element that forms compounds with the alkali metals at ambient pressure is Au. It has the highest electronegativity of any metal and lies to the right of a broad peak in charge density in the transition series, which is centered near the metals Fe, Ru, and Os (Fig. 1). Under pressure, because of the *s*-to-*d* transition, the charge densities of the alkali metals increase much more rapidly than those of the transition metals. Therefore, the boundary separating the metals that do react with the heavy alkali metals under ambient pressure (for example, Zn, Cd, and Au) from those that do not (the transition series) should move to the left in the periodic table with increasing pressure (Fig. 1). In agreement with these predictions, we have found that at relatively low pressures (2 to 5 GPa), K and Ag (just to the left of Cd in the periodic table) react to form many compounds at room temperature (*13*).

The first metal in the third row of the periodic table that has a charge density large enough to form compounds with Fe is Sc. Because there is a relation between the bulk modulus and molar volume of a metal and its charge density (*14*), the effect of pressure on the charge density can be estimated from the equation of state for the metal. By 30 GPa, the bulk modulus of K (81 GPa) exceeds that of Sc at ambient pressure (54.6 GPa), and the charge density

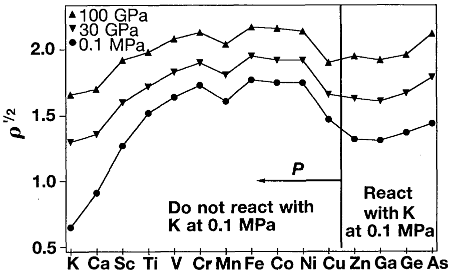

Fig. 1. Cube root of the Miedema charge density parameter for metals in the third row of the periodic table. The charge densities are derived from the bulk moduli and the volumes of the metals at high pressure, which were determined from experimental equations of state (*1, 14*). The vertical line represents the boundary between the metals that react with Na, K, Rb, and Cs at 0.1 MPa and those that do not.

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