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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21. We thank A. M. Boullier for advice during fluid and melt inclusion characterization, J. C. Demange for the care and rapidity with which he set up the mass spectrometer, and X. Framboisier who provided assistance during the analysis. This work benefited from discussions with J. Ludden and M. Ozima and from internal review by I. N. Tolstikhin. This is Centre de Recherches Pétrographiques et Génchimiques–CNRS contribution 1200.

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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

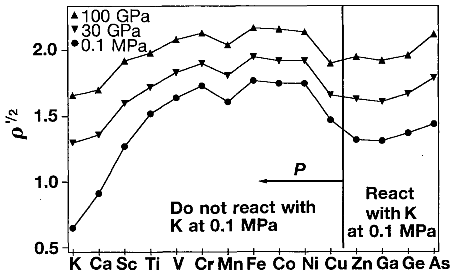

Fig. 1. Cube root of the Miedema charge density parameter for metals in the third row of the periodic table. The charge densities are derived from the bulk moduli and the volumes of the metals at high pressure, which were determined from experimental equations of state (*1, 14*). The vertical line represents 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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of K is also larger (Fig. 1). Thus, like Sc at ambient pressure, K should begin to react with Fe and neighboring transition metals (Co and Ni) at sufficiently high pressures.

We have developed techniques to investigate the formation of compounds between alkali metals and transition metals under pressure using a laser-heated diamond anvil cell. Elemental K and Ni powder were loaded in a molar ratio of 2:1 into a Mao-Bell diamond anvil cell. A thin ($\sim$10 μm) single-crystal sapphire window was placed between the sample and the front diamond to thermally insulate the anvil from high temperatures (*15, 16*). The sample was then compressed to 31 GPa and laser-heated through the front diamond (estimated temperature $\sim$2500 K) with 1053-nm radiation from a 32-W neodymium–yttrium lithium fluoride laser. The sample pressure was measured by means of ruby fluorescence (*17*). Diffraction patterns were collected at high pressures before and after laser heating (*18*). Before laser heating (Fig. 2), the diffraction pattern of the sample was characteristic of a mixture of K [in the high-pressure phase K(III) (*3, 19*)] and Ni. After laser heating, the diffraction lines due to K(III) completely disappeared and new diffraction lines appeared, indicative of reaction between K and Ni to form an intermetallic compound. The pressure was then increased to 37 GPa, and the sample was heated again. After the second heating, some of the new lines in the diffraction pattern had greater intensity and were sharper. The strong intensity of the lines shows that an appreciable fraction of the sample reacted. The new lines can be indexed by a tetragonal unit cell with dimensions a = 9.65 Å and c = 9.26 Å (Table 1) (*20*). We performed several more experiments with a different molar ratio of K to Ni (3:1) that exhibited a diffraction pattern with many other new lines, indicating the formation of other compounds with different compositions. These results demonstrate that, as a *d*-electron element, K has a very different chemistry than as an *s*-electron element (*21*).

The techniques used here may allow the synthesis of alkali metal–transition metal compounds that are quenchable in metastable form to much lower pressures. When the pressure of the sample was released to 3 GPa, diffraction lines of a K-Ni phase together with diffraction lines due to elemental K appeared (Fig. 3). The interplanar spacings of the K-Ni phase can be indexed with a cubic unit cell that follows the extinction rules for body-centered symmetry. The unit cell parameter a = 4.55 Å is significantly smaller than the unit cell at this pressure of pure body-centered cubic (bcc) K, 4.62 Å (Table 2). This result indicates that a substitutional solid solution of K and Ni, in which K may retain its *d*-electron character, is present at a pressure much lower than the synthesis pressure.

These observations may have significant implications for the chemistry of Earth's core. Seismological measurements show that Earth's core is less dense than pure Fe at core temperatures and pressures, implying that there must be a substantial amount of a light element incorporated into the core (*11*). Elements such as K, H, C, S, O, and Mg have been proposed as core constituents to explain the reduced density. Incorporation of radioactive elements such as U, Th, and the ^{40}K isotope of K in the core could serve as a source of radiogenic heat, affecting the heat distribution within Earth and the geodynamo (*10*). Because the charge densities of Fe and Ni are similar despite the slightly lower electronegativity and work function of Fe (*12*), Miedema's rules predict that reaction of Fe and K should occur below core pressures (136 to 360 GPa). The incorporation of K and other light elements in the core is dependent on the processes that occurred during accretion (*11*); however, in view of the pressure-induced chemistry documented here, the presence of K in the core remains a viable hypothesis.

Our results may also be important for understanding partitioning of trace elements between the core and mantle, a key problem in mantle-core geochemistry and the evolution of Earth (*22*). Although the effects of temperature on partitioning have been explored theoretically and experimentally, the effects of very high pressures on partition coefficients remain largely unconstrained. At ambient pressure the solubility of alkali metals in transition metals such as Ni and Fe is very small (*23*). Our results demonstrate that the effect of pressure on partitioning could be large and cannot be determined from extrapolation of low-pressure data.

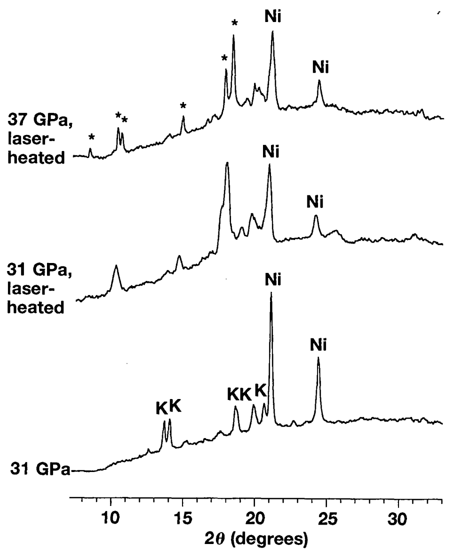

Fig. 2. X-ray diffraction patterns before and after laser heating of the K-Ni mixture. New diffraction lines appeared after laser heating (marked by asterisks) that are indicative of the formation of a new phase. In this experiment no diffraction lines were observed from the sapphire insulator because it was a single crystal.

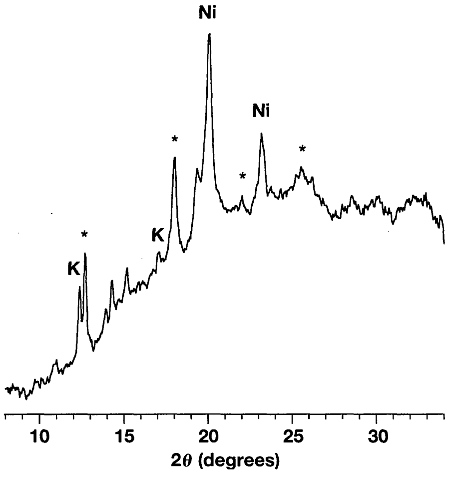

Fig. 3. X-ray diffraction pattern for the K-Ni sample after quenching to 3 GPa. Diffraction lines due to the presence of a solid solution (marked by asterisks) are present.

Table 1. Observed interplanar spacings d of the diffraction pattern obtained from the laser-heated K-Ni sample at 37 GPa. The interplanar spacings are tentatively indexed by a tetragonal unit cell (a = 9.65 Å, c = 9.26 Å).

d_{obs} (Å)	d_{calc} (Å)	Δ_d (Å)	$hk\ell$
4.84	4.83	0.01	200
3.92	3.91	0.01	211
3.83	3.83	0.00	112
2.743	2.748	0.005	222
2.292	2.290	0.002	223
2.227	2.227	0.000	303
1.941	1.942	0.001	Ni
1.683	1.682	0.001	Ni

Table 2. Observed interplanar spacings d for the K-Ni sample after quenching to 3 GPa. The indices and calculated interplanar spacings for the K-Ni solid solution (a = 4.55 Å) and for bcc K at 3 GPa (a = 4.62 Å) are given.

d_{obs} (Å)	d_{calc} (Å)	Δ_d (Å)	$hk\ell$
3.29	3.27	0.02	K
3.22	3.22	0.00	110
2.396	2.311	0.085	K
2.272	2.275	0.003	200
2.036	2.026	0.010	Ni
1.857	1.857	0.000	211
1.857	1.886	0.029	K
1.764	1.754	0.010	Ni
1.608	1.608	0.000	220

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6. By a pressure of 4.2 GPa, after the *s*-to-*d* transition has begun, Cs collapses in volume by a factor of 3 and undergoes a phase transition from a close-packed structure to an open, body-centered tetragonal crystal structure [Cs(IV)] as a result of the more covalent, directional nature of the bonding involving large *d* orbitals (*4*). Cesium also becomes a superconductor at this pressure [J. Wittig, *Phys. Rev. Lett.* **24**, 812 (1970)]. *d* electrons have little electron density at the nucleus and, unlike other transition metals, Cs(IV) has no valence *s* electrons. As a result, the bonding in Cs(IV) is unusual, with minimal valence electron density at the nucleus and maximum electron density between the atoms. This hypothesis is confirmed by electronic structure calculations that show that Cs(IV) can be considered an electride, consisting of Cs^+ ions and interstitial electrons [H. G. von Schnering,and R. Nesper, *Angew. Chem. Int. Ed. Engl.* **26**, 1059 (1987)]. The other heavy alkali metals, K and Rb, also exhibit large changes in electronic structure and bonding under pressure (*1*).
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13. T. Atou, L. J. Parker, J. V. Badding, unpublished data. Phases with stoichiometries Ag_2K, AgK_2, and AgK_3 were found.
14. The charge density at the Wigner-Seitz radius can be determined from $n_{WS} = 0.82\,(K/V_m)^{1/2}$, where K and V_m are the bulk modulus (in gigapascals) and molar volume (in cubic centimeters), respectively, at a given pressure (*12*). Because the Miedema charge density parameters are adjusted empirically from experimental values (*12*), we estimated the charge densities at high pressure by adding a shift in charge density under pressure determined from this equation to the Miedema value at ambient pressure.
15. Use of a single-crystal sapphire, which has great thermal and chemical stability, greatly retards or eliminates reaction between transition metals and the insulating medium in laser-heating experiments [G. Shen, P. Lazor, S. K. Saxena, *Phys. Chem. Minerals* **20**, 91 (1993); R. Boehler, *Nature* **363**, 534 (1993)]. Reaction between elemental K and clean sapphire plates can also be ruled out on thermodynamic grounds.
16. Because K is very reactive, we took care to avoid introduction of water and oxygen impurities. Samples were loaded in a Vacuum Atmospheres glove box with a very high purity Ar atmosphere (~1 to 2 ppm O_2-H_2O). Before loading, the diamond cell, gasket, and sapphire crystals were heated to drive off any water or other adsorbed contaminants, then quickly loaded into the glove box while hot.
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21. It is reasonable to expect that the large changes that occur in the size and electronic structure of the alkali metals under pressure will affect their behavior in other interesting or important chemical systems. For example, thermodynamic calculations indicate that formation of the compound CsF_2, which would involve bonding to electrons in a noble gas configuration octet, should be favored under high pressure (J. V. Badding, unpublished data). The availability of the *d*-electron bonding state of the alkali metals should also allow new chemistry with many of the nonmetallic elements.
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Detrital Zircon Link Between Headwaters and Terminus of the Upper Triassic Chinle-Dockum Paleoriver System

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New detrital-zircon geochronologic data reveal that a through-going paleoriver connected Texas with Nevada in Late Triassic time. Sandstone from the Upper Triassic Santa Rosa Sandstone (Dockum Group) from northwestern Texas contains a detrital zircon suite nearly identical to that found in western Nevada in the Upper Triassic Osobb Formation (Auld Lang Syne Group, correlative with the Chinle Formation). The Santa Rosa Sandstone was derived in large part from the eroded Cambrian core of the Amarillo-Wichita uplift, as evidenced by abundant zircons with ages of 515 to 525 million years. Other zircon grains in the sandstone are Permian, Devonian, Proterozoic, and Archean in age and, with the exception of the Archean grain, are also matched by the population in the Nevada strata.

The sources and paths of ancient river systems are generally traced by distinctive grains (*1*), paleocurrents, and facies correlations, but these arguments provide no unique ties between source areas and sites of deposition. Distinctive clasts have been used with some success (*2*), but are of use only where coarse gravelly detritus is preserved. It remains uncertain whether an ancient river can be traced successfully from headwaters to terminus by such potentially ambiguous means.

The Upper Triassic Chinle Formation of the Colorado Plateau is a succession of continental deposits that originally extended across much of western North America (*3*, *4*) (Fig. 1). Lithologically similar and stratigraphically equivalent rocks of the same age in the Dockum Group of eastern New Mexico and northwestern Texas contain paleocurrents that suggest transport into the Chinle basin, and a connection between the two units has been proposed on that basis (*4*). We use single-zircon U-Pb data from the basal Dockum Group, together with published data from the Chinle Formation and its correlatives in Nevada (*5*), to trace a through-going river system between Texas and Nevada in Late Triassic time (Fig. 1).

The Santa Rosa Sandstone is the basal formation of the Upper Triassic Dockum Group, which is widely exposed around the perimeter of the southern High Plains and is in the subsurface of west Texas and eastern New Mexico (*6*). The Santa Rosa Sandstone rests unconformably on Permian rocks and locally on Middle Triassic rocks [Anton Chico Formation (*7*)] and is as much as 40 m thick. The sandstone is com-

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