The deepest rocks known from within Earth are fragments of normal mantle (~400 km) and metamorphosed sediments (~350 km), both found exhumed in continental collision terranes. Here, we report fragments of a highly reduced deep mantle environment from at least 300 km, perhaps very much more, extracted from chromite of a Tibetan ophiolite. The sample consists, in part, of diamond, coesite-after-stishovite, the high-pressure form of TiO₂, native iron, high-pressure nitrides with a deep mantle isotopic signature, and associated SiC. This appears to be a natural example of the recently discovered disproportionation of Fe²⁺ at very high pressure and consequent low oxygen fugacity (fO₂) in deep Earth. Encapsulation within chromitite enclosed within upwelling solid mantle rock appears to be the only vehicle capable of transporting these phases and preserving their low-fO₂ environment at the very high temperatures of oceanic spreading centers. Results and Discussion Terrestrial Nitrides and Single Crystals TiO₂ II as Inclusions in Coesite. We now report high-pressure nitrides, oxides, and native Fe occurring as submicroscopic inclusions (50–200 nm) within coesite from the small rock fragment of ref. 8 (Fig. 1). The prismatic external form of the polycrystalline coesite domains that host these inclusions establish that the coesite formed by pseudomorphic replacement of stishovite (minimum pressure for its stability ~10 GPa, implying >300-km depth) (8). With a focused ion beam (FIB) instrument, we prepared several thin foils from this material that were examined in the transmission electron microscope (TEM), leading to discovery and characterization of the additional phases. Further analysis by nanometer-scale secondary ion mass spectrometry (NanoSIMS) determined the N and C isotopic compositions. At the scale of the TEM, titanium nitride (TiN) is abundant within coesite and is accompanied by cubic boron nitride (c-BN) (Fig. 2 A and B) and less-abundant crystals of native Fe (Fig. 2 C) and sporadic inclusions of TiO₂ II (Fig. 2 E), a high-pressure polymorph of rutile with the αPbO₂ structure (Fig. 2 F) (15), and boron carbide of unknown stoichiometry. Electron diffraction analysis established the cubic symmetry of both nitrides, with a = 4.25 Å for TiN (Fig. 2D) and a = 3.61 Å for BN (Fig. 2B). TiO₂ II unit cell parameters were: a = 4.49 Å, b = 5.47 Å, c = 4.91 Å (Fig. 2F). Initial identification of nitrides was accomplished by X-ray energy dispersive spectroscopy (EDS) but overlapping peaks of N K-peak and Ti Kα and Kβ peaks, and N K-peak and B-K peak in this region of the spectrum, make such analysis qualitative at best. As a consequence, we analyzed both TiN and BN with electron energy loss spectroscopy (EELS) in the TEM and confirmed the identifications (Fig. 3). The EELS analysis confirms the 1:1 atomic ratio of both TiN and BN. Element
mapping showed that Ti, B and N are restricted to the nano-inclusions, whereas Si and O characterize the host coesite (Fig. 4).

Using a ∼100-nm-diameter Cs⁺ primary beam, the isotopic compositions of N and C were measured by NanoSIMS on these same foils; the elemental distributions of N, C, and Si were also determined. A comparison of TEM images with NanoSIMS ¹²C¹⁴N isotope maps (nitrogen is detected as the CN molecule) demonstrates that TiN and c-BN are the only phases containing significant nitrogen (Fig. 5). With the exception of rare small (<50 nm) boron carbide grains intergrown with TiN and BN, carbon is much less abundant than nitrogen; it is found primarily as solid solution in TiN. Four replicate analyses of the largest available region of TiN (∼2 × 8 μm) yielded isotopic compositions of δ¹⁵N = -10.4 ± 3.0‰ and δ¹³C = 5 ± 7‰; uncertainties are two standard errors. No variations in N and C isotope compositions were detected outside analytical uncertainty. The large uncertainty in δ¹³C reflects the very small amount of C in the TiN and consequent low number of C ions collected.

Natural osbornite (TiN) is very rare on Earth (16, 17) and has never been found in situ; it is reasonably common in meteorites, especially iron meteorites (18). However, neither boron nitride nor boron carbide have previously been found in nature. TiO₂ II has been reported from two terrestrial localities (19, 20); in both cases it is preserved only in a special low-energy environment along a single twin boundary of a retrograde rutile crystal. Here, we found it as isolated crystals with no evidence of reversion to rutile. The presence of TiO₂ II, by itself, confirms the 10-GPa minimum pressure necessary to stabilize stishovite because at 1,300 °C, certainly a minimum temperature for a mantle upwelling at 300 km, rutile is stable to 10 GPa (15).

Low Oxygen Fugacity (fO₂) in the Luobusa Chromite. Another perplexing aspect of this problem is the very low fO₂ conditions of these materials, including SiC (12), although the latter is not incorporated in this particular specimen. Recent experimental work has shown that, under conditions of the lower mantle (21, 22) and even deep upper mantle (23), ferrous ion disproportionates into ferric ion + Fe metal. Thus, it may be that only the outermost shell of Earth [perhaps as thin as ∼250 km (23)] is strongly oxidized and that it should be expected that rocks/minerals brought to shallow levels from great depth could arrive highly reduced if protected during their last few hundred kilometers of travel. In the case under discussion here, the abundant evidence for shallow mantle processes active at higher fO₂ in this and other ophiolites means that the reduced conditions recorded in the sample discussed here had to be preserved by shielding from the shallow environment by encapsulation within chromite. That this could occur at the very high temperatures characteristic of oceanic spreading environments is surprising.

The Luobusa chromites provide information that is consistent with this hypothesis. The chromite of the massive deposit that carries the signal of very low fO₂ (including the presence of native Fe), shows a high Fe³⁺/ΣFe = 39 ± 1%, whereas it is Fe³⁺/ΣFe = 21 ± 1% in the disseminated ore that clearly has been affected by shallow processes. The electron microprobe chemical analyses revealed the following composition of chromites hosting the exotic inclusions described herein: (n = 3,
wt%) MgO = 15.62, Al₂O₃ = 11.04, TiO₂ = 0.16, Cr₂O₃ = 60.43, ΣFeO = 12.10, NiO = 0.18, total = 99.53. Mossbauer data collected by T. Ruskov (Institute for Nuclear Research and Nuclear Energy, Sofia, Bulgaria) from the same chromite grains yield Fe³⁺/ΣFe = 39 ± 1%; the calculated chemical formula of chromite is \((\text{Fe}^{2+}_{2.01} \text{Fe}^{3+}_{0.08} \text{Mg}^{2+}_{0.72})_{1.9} (\text{Cr}_{1.53} \text{Al}_{0.41} \text{Ti}_{0.01} \text{Fe}^{3+}_{2.02})_{1.99} \text{O}_{4}\). On the one hand, because this chromite contains a high fraction of Fe³⁺, by conventional interpretation it implies a highly oxidized environment. However, this Fe³⁺-rich chromite contains Fe⁰ (native Fe) and other metals and highly reduced metal nitrides that are stable at high pressures and high temperatures (24, 25) and show no evidence of low T alteration (Fig. 2 A and B). It also contains inclusions of the ultrahigh-pressure (UHP) phases TiO₂ II (described herein) and exsolution lamellae of coesite and diopside (9), suggesting that a precursor of such chromite could be a high-pressure polymorph of chromite (26). Given the totality of these observations, we suggest that the resolution of conflicting fO₂ indicators is that in the deep mantle (>300 km) the fO₂ is low and the elevated abundance of Fe³⁺ is a consequence of crystallographic constraints imposed by high-pressure host phases. Upon decompression and stabilization of upper-mantle minerals with abundant Fe²⁺ sites, the Fe³⁺ and Fe⁰ react in the reverse direction of the Fe²⁺ disproportionation proposed by (21)

\[2\text{Fe}^{3+} + \text{Fe}^{0} \rightarrow 3\text{Fe}^{2+},\]

and, if all Fe⁰ is consumed, the fO₂ rises to the observed values of the upper mantle. In the present case, this reaction took place...
outside of chromite but the low FeO was preserved within massive chromite because of the abundant reduced phases within a highly restricted, refractory, chemical environment.

Our Mössbauer studies result looks exactly like the disproportionation of Fe$^{2+}$ in the experiments discussed above, suggesting that at some time in the early history of the chromitite, perhaps in the stability field of a high-pressure polymorph, crystallographic constraints on the number of Fe$^{3+}$ sites in the chromite polymorph have simultaneously increased the abundance of ferric iron and stabilized native iron, dropping the overall oxygen fugacity. If so, these rocks may be the first recognized natural example that the deep mantle may be characterized by phases that enforce disproportionation of Fe$^{2+}$ and low FeO. Upwelling of such rocks to the surface where ferrous sites are abundant and ferric sites rare in mantle phases would lead to oxidation except in rare cases, such as this one, where local isolation has retained the low FeO and consequently the deep mantle phases. Detailed examination of chromitites worldwide and high-pressure experimentation on Cr-rich systems are both required to address these possibilities.

In addition to these indicators suggestive of very high pressure, the exsolution lamellae of coesite and diopside from chromite (9) show that at some time in the history of this deposit both SiO$_2$ and CaMg$_3$Si$_2$O$_6$ were soluble to a significant extent in chromite or its predecessor. The knowledge that chromite bulk chemistry can be stable to $>$20 GPa through at least two high-pressure polymorphs (26), and the experimental demonstration that the SiO$_2$ solubility in spinel-structured phases increases greatly at very high pressures (27), are consistent with the hypothesis that at least part of the massive chromite ore at Luobusa has a very deep origin and its refractory nature has shielded relics of such depths from obliteration by shallow processes.

**How Great Might the Depth of Origin Be?** We can set a minimum depth of 300 km for the origin of this material through the presence of TiO$_2$ II and former presence of stishovite, but we cannot yet constrain the maximum depth. For example, the upper limit of stishovite stability is $\approx$80 GPa (28); TiN is stable to at least 40 GPa (24) and c-BN to at least 60 GPa (25, 29). Kyanite is stable only to $\approx$15 GPa, where it breaks down to corundum + stishovite (30), but the reverse reaction could have accompanied decompression events, similar to stishovite inversion to coesite. Chromite is stable only to 12 GPa, but chromite stoichiometry is stable to at least 20 GPa (26). Thus, the origin of these materials can have been either from the deep upper mantle or the lower mantle.

**Geophysical Significance of Nitrides and Related UHP Phases.** In attempting to understand these observations in greater detail, two major questions remain: What is the significance that this finding of nitrides and other UHP minerals in mantle rocks occurs in a zone of upwelling; especially, where does the N come from? How can coesite and TiO$_2$ II be preserved within these high-temperature rocks with absolutely no evidence of reaction to their low-pressure polymorphs, quartz and rutile, respectively?

The geological setting of the host ophiolite strongly suggests nitrogen in the nano-inclusions is mantle-derived. The systematic N isotope distribution in Earth are complex but most upper-mantle rocks exhibit a consistent signature of $\delta^{15}$N = $-5 \pm 2\%$o, implying a globally uniform reservoir (31). Exceptions to this uniformity are sporadic much more negative values, e.g., $\delta^{15}$N = $-25\%$o in Fuxian diamonds (32) and $\delta^{15}$N as low as $-24\%$o for some mid-ocean ridge basalt (MORB) samples (33). In contrast to these negative values from the mantle, the atmosphere, ocean, and crust are all characterized by positive values of $\delta^{15}$N: 0$+5\%$o for the atmosphere and ocean and 5$+12\%$o for the crust (granites, metamorphic rocks, and sediments) (31). It has been recently found that ocean island basalt magmas thought to come from the bottom of the upper mantle or the lower mantle have $\delta^{15}$N values in the same range as continental materials (31). Similarly, a study of SiC in kimberlites of Russian Siberia (34) found crustal values of $\delta^{15}$N and highly negative values of $\delta^{13}$C. Both of these observations suggest N from subducted continental material and the C isotopes are consistent with subducted organic carbon.

Our isotopic results, with $\delta^{15}$N = $-10 \pm 3\%$o, are inconsistent with a continental origin for the N, despite the fact that the material discussed here (rich in SiO$_2$ and Al$_2$O$_3$ and carrying boron and some alkalies) is chemically incompatible with mantle rocks, at least at pressures within the upper mantle, thereby suggesting an origin from subducted continental material or oceanic sediments. The $\delta^{15}$N results are slightly more negative than most uppermost mantle N, but they are in the same direction as other, more negative, outliers. We conclude that this is mantle N, perhaps from an old and/or deep mantle reservoir. There is intriguing literature addressing the possibilities for N incorporation into the deep Earth as nitrides. It includes finding ilmenite xenocrysts in an African kimberlite containing 2.5 wt% N in their structure (35) (or, given our results, perhaps as included nitrogen), a hypothetical prediction that TiN should be a mantle phase that binds nitrogen “missing” after Earth accretion (33), and synthesis of Fe-nitrides at extreme pressures and temperatures as a possible candidate for light element partitioning in formation of the core (36). The results of this study support the concept of deep nitrides and suggest that the source is not caused by recycling from the surface. They also suggest that other materials showing evidence of origin from great depths deserve systematic testing for N. A focus on the role of nitrogen might bring unexpected developments in understanding of our planet’s history.

Our carbon isotopic results ($\delta^{13}$C = $5 \pm 7\%$o) are nominally high for normal mantle C, but the large statistical error in the numbers makes it impossible to argue for significance of this observation. However, our results are clearly inconsistent with the strongly negative values of subducted organic carbon, leaving us with an inconsistency between the major element chemistry (and boron) of this rock fragment (that simple logic would suggest is continental in nature) and the volatile content. Either there is a way to explain the SiO$_2$- and Al$_2$O$_3$-rich, B- and alkali-bearing bulk chemistry as being compatible with a mantle origin, or we must conclude that the volatiles were added later in the history of this rock. Significantly more negative values found, e.g., in diamonds from Fuxian, China ($\delta^{15}$N = $-25\%$o) (32) and sporadic similar values reported from MORB (33, 37) suggest there is a reservoir at greater depth with more negative $\delta^{15}$N values that also could be the explanation for our data. How such N could get into this material depends strongly on how deep is the origin of the host chromitites and what is the origin of the extremely low FeO within them.

Last, how can one explain the unaltered state of coesite and TiO$_2$ II at low pressure and high temperature? At temperatures appropriate for mantle upwelling at ocean spreading centers, TiO$_2$ II is stable only at pressures within the stishovite stability field ($>10$ GPa) (15). Nevertheless, neither the TiO$_2$ II nano-inclusions nor the host coesite show any evidence of reaction to their low-pressure polymorphs, rutile and quartz, respectively. These observations contrast sharply with the observation that in UHP rocks from continental collision zones; relict coesite is heavily reacted to quartz and TiO$_2$ II is restricted to low-energy sites along rutile twin boundaries (19, 20). Preservation in such a pristine state in this ophiolite must reflect an extraordinarily low local fH$_2$O, which is consistent with the very low FeO indicated by the coexisting phases.
Summary. The observations reported here show that nitrides, oxides, and metals encapsulated within massive chromite of an ophiolite carry a record of formation at very high pressure and temperature, and very low $F_O_2$. Given that these materials came to near the surface at a temperature near 1,300°C, they must have been at least that hot at their depth of formation, 300 km (pressure > 10 GPa). Although we still lack a full explanation of these findings, the fact that chromite of a second ophiolite also has been found to contain abundant diamonds and other exotic, reduced phases (10) verifies that chromite inclusions of at least some ophiolites offer another window into the deep mantle and the distribution of nitrogen in Earth.

Methods and Analytical Techniques

FIB Sample Preparation. Electron transparent foils were prepared with the FIB instrument (FEI FIB200) from selected areas. The foils were milled normal to the surface of the carbon-coated thin section, thereby excluding any surface contamination of the TEM foil. The foil was $15 \times 10 \times 0.150 \mu m$. Details of the FIB method are in ref. 38.

TEM. TEM investigations were performed with a TECNAI F20 XTWIN TEM operating at 200 kV with a field emission electron source. The TEM is equipped with a Gatan Tridimen filter, an EDAX Genesis X-ray analyzer with ultra-thin window, and a Fishione high-angle annular dark-field detector. Tridimen filter was used for the correction of energy-filtered images, applying a 2 eV window to the zero loss peak. EELS spectra were acquired with a dispersion of 0.1 eV/channel and an entrance aperture of 2 mm. The resolution of the filter was 0.9 eV at half-width, at full maximum of the zero loss peak. Spectra were acquired in the diffraction mode. Acquisition time was 1 s. Spectra processing (background subtraction, removal of plural scattering) was performed by using the DigitalMicrograph software package. EDS spectra were usually acquired in the scanning transmission mode by using the TIA software package. EELS spectra were acquired with a dispersion of 0.1 eV, and acquisition time was 60 s.

NanoSIMS. SIMS of FIB sections was performed at the Lawrence Livermore National Laboratory by using a Cameca NanoSIMS 50 instrument. A Cameca NanoSIMS 50 instrument. A normal incidence electron flood gun was used for charge compensation. There were two sets of measurements: (i) the $^{15}N/^{14}N$ value reported above comes from measurements of C and N abundances on the uncoated foils; (ii) because of the low intensity of $^{15}N$ ions, a $25-50$-nm thick carbon coat was deposited onto the foil to compensate for the low abundance of $^{15}N$ in the TiN and maximize the formation of $^{15}N$-secondary ions. With this procedure, the $^{15}N/^{14}N$ intensity increased substantially to $\approx 500,000$ m$^{-3}$ at the onset of each analysis. The data were corrected for instrumental mass-dependent fractionation of C and N based on analyses of National Institute of Standards and Technology (NIST) SRM-8588 (potassium nitrate) mixed with NIST SRM-8541 (graphite) and Bacillus subtilis endosperm samples of known $^{15}N$ and $^{15}O$ (39). The difference in chemical composition between the C-rich nitrogen isotope standards and the Ti-rich, C-poor TiN raises a potential concern over the accuracy of the mass-dependent fractionation correction. Although a full evaluation requires a TiN standard with well-determined $^{15}N/^{14}N$, the absence of significant variations in instrumental mass-dependent fractionation for a variety of N-bearing materials supports the approach followed here. Data were processed as quantitative isotopic ratio images by using custom software (L’image; L. Nittler, Lawrence Livermore National Laboratory) and were corrected for detector dead time and image shift from layer to layer. Regions of interest (ROIs) were defined based on elemental composition correlated with TEM imaging of the FIB sections, and the isotopic composition for each ROI was calculated by averaging over the replicate layers.

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