Atomic-Scale Environment of Re and Radiogenic ^{187}Os in Natural Molybdenite Mineral Related to Reliable Re-Os Dating

The age of terrestrial and extraterrestrial materials is determined by the ratio of parent to daughter nuclides, which can vary as a function of time due to radioactive decay [1]. The radiometric dating method assumes the retention of both parent and daughter nuclides in the samples since their formation. The chemical properties of the daughter nuclides often differ from those of the parent, which may result in the separation of the parent and daughter nuclides. Therefore, their retention in the sample may depend on the chemical environment of both nuclides, which affects their stabilities against various processes such as metamorphism, alteration, and diffusion within a crystal. Therefore, the chemical states of parent and daughter nuclides in mineral or rock samples is important for accurate dating.

Recently, Os geochemistry has attracted considerable interest due to the variation of Os isotopes related to the ^{187}Re-^{187}Os decay system [2]. In particular, molybdenite (MoS_2) is known as a robust geochronometer resistant to regional deformation and metamorphism, as demonstrated by a trial of the ^{187}Re-^{187}Os system for the dating of molybdenite [3]. In this method, however, it has been indicated that successful dating requires the careful selection of a representative sample from a specific geologic occurrence with a sufficient volume of the sample for the analysis to overcome the decoupling of ^{187}Os and Re in the molybdenite after their formation. This decoupling of Re and Os has been attributed to the high mobility of radiogenic ^{187}Os relative to Re in molybdenite. In this study, we examine the local structure of Re and radiogenic ^{187}Os at the atomic scale in molybdenite using their X-ray absorption fine structure (XAFS) to clarify the atomic-scale environment and chemical state of the parent and daughter nuclides (Fig. 1) [4]. The XAFS for Os in molybdenite is considered to originate from radiogenic ^{187}Os produced by the β-decay of ^{187}Re (half life: 4.4×10^{10} years), since it is well known that the abundance of common Os initially contained in molybdenite is negligible. Thus, the local atomic structures of Re and radiogenic ^{187}Os in molybdenite from the Onganja Mine (Namibia) were examined by XAFS, which was conducted at beamlines **BL37XU** and **BL01B1**.

Rhenium L_{III}-edge XANES (X-ray absorption near-edge structure) and EXAFS (extended X-ray absorption fine structure) showed that the oxidation state of Re, the interatomic distances between Re and the neighboring atoms, and the coordination number of Re to S are very similar to those of Mo in molybdenite. The results confirm that Re is substituted at the Mo site in molybdenite.

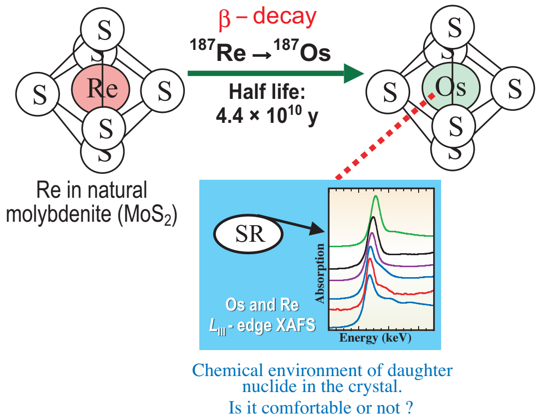

Fig. 1. Schematic representation of this study illustrating the importance of determining the chemical environment of the daughter nuclide (^{187}Os in this study) in the mineral (molybdenite in this study) for the reliable dating of natural samples.

We successfully measured the L_{III}-edge XANES and EXAFS of the small quantity (8.55 ppm) of radiogenic Os in molybdenite in fluorescence mode by removing the interference of X-rays from Re and other elements using a crystal analyzer system at BL37XU (Fig. 2) [4,5]. The XANES data indicate that the oxidation state of radiogenic Os is either Os(IV) or Os(III), similar to Re(IV) and Mo(IV), but not Os(II), the state in $Os^{II}S_2$ (= erlichmanite), naturally occurring stable Os sulfide (Fig. 3). XANES data also suggest that radiogenic Os does not form a secondary Os phase, such as OsS_2 or Os metal, in molybdenite.

The EXAFS of radiogenic Os in molybdenite was successfully simulated assuming that Os is present at the Mo site in molybdenite using the parameters

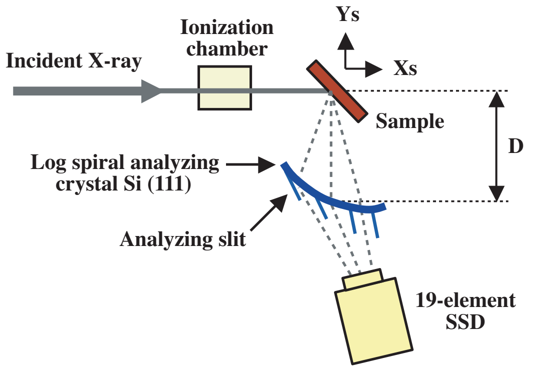

Fig. 2. Schematic of experimental setup of the fluorescence XAFS using a crystal analyzer system at BL37XU.

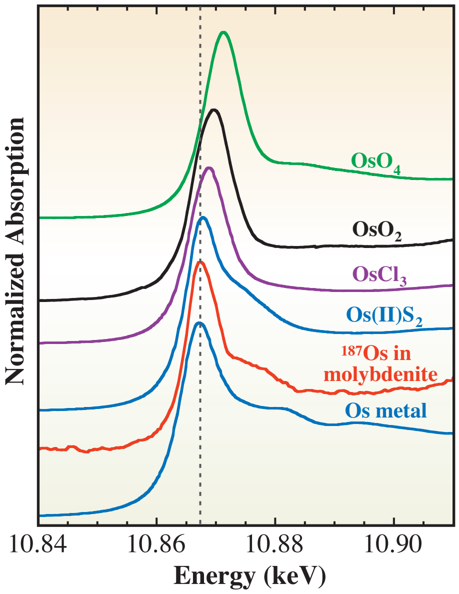

Fig. 3. Osmium L_{III}-edge XANES for Os in molybdenite and reference materials such as Os metal, $Os^{II}S_2$, $Os^{III}Cl_3$, $Os^{IV}O_2$, and $Os^{VIII}O_4$.

generated by FEFF (Fig. 4). EXAFS data are not consistent with the presence of Os phases such as Os metal and OsS_2. The EXAFS simulation showed that the interatomic distance between Os and S is 2.27 Å, which is 0.12 Å smaller than those of Re-S and Mo-S (2.39 Å) in the molybdenite. This shorter distance between radiogenic Os and S may be explained by the relatively small ionic radii of Os(IV) and Os(III). The interatomic distance of Os-S is 2.35 Å in $Os^{II}S_2$, and Os(III) or Os(IV) should have a shorter interatomic distance with S than that in $Os^{II}S_2$ due to the larger charge. The similar valence and ionic radius between Re and Mo in molybdenite obtained from our XAFS data support the fact that a large amount of Re can be incorporated into the Mo site, as was indicated in previous studies (e.g., [3]), while the different geochemical properties of Os compared with Mo and Re suggested here are evidence for the much lower abundance of common Os in molybdenite [3]. This makes molybdenite an ideal mineral for the Re-Os geochronometer. However, the shorter distance between radiogenic Os and S compared with those of Re-S and Mo-S in molybdenite suggests that Os diffuses faster than Re and Mo ions in molybdenite, which may induce the decoupling of Re and radiogenic Os in molybdenite. This is consistent with the higher mobility of Os than Re in molybdenite suggested in previous studies.

To our knowledge, this is the first study to clarify the chemical environment at atomic scale for the daughter nuclide produced by radioactive decay in natural samples. Atomic scale information is essential for every decay system to elucidate reliable dating data to understand the evolution of the solar system and the earth.

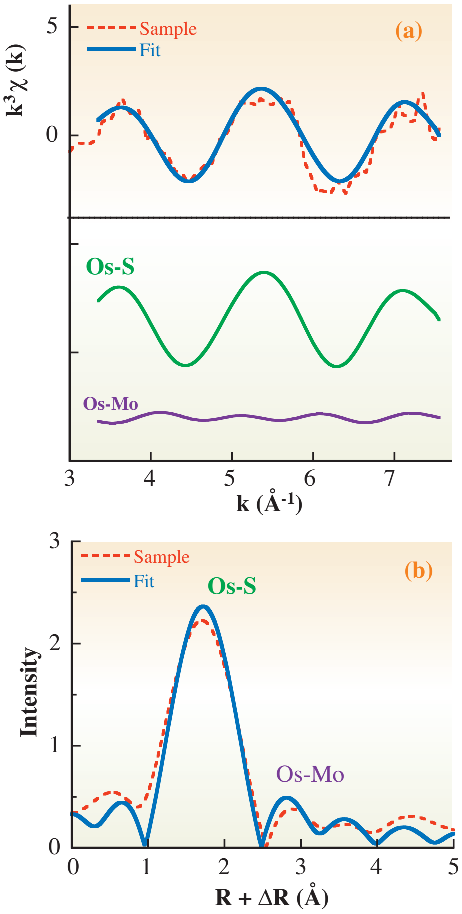

Fig. 4. EXAFS results for Os in molybdenite including **(a)** k^3-weighted $\chi(k)$ with the simulated spectrum with the contribution of Os-S and Os-Mo shells considered therein and **(b)** radial structural function (RSF) for Os with the simulation curve.

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