In situ Observation of Liquid Immiscibility in the Fe-O-S System at High Pressures and Temperatures

The Earth's liquid outer core consists of a liquid Fe-Ni alloy with 10% comprising light elements. Oxygen and sulfur are possible elements in the outer core according to geochemical arguments. Recently, seismological observations show P-wave velocity reduction 100 km underneath the core-mantle boundary, which means that an outermost layer may exist at the top of the outer core (Fig. 1) [1]. The layer may have formed if excess oxygen had been exsolved from an Fe-O-S liquid as an Fe-O ionic liquid during the cooling of the Earth. Experimental studies on phase relations in the Fe-O-S system show liquid immiscible regions at high pressures [2,3] that are composed of Fe-S metallic and Fe-O ionic liquids. The outermost core layer is closely related to the evolution of the growing Earth and the flow of the core is associated with the geodynamo.

In previous studies on the Fe-O-S and Fe-O systems (e.g., Refs. [2,3]), investigations of liquid immiscibility were based on the textural observations of the quenched products. Liquid immiscibility should be interpreted carefully because a miscible liquid passes through the stability field of immiscible liquids during quenching (e.g., Ref. [4]). Therefore, it is important to directly determine the stability fields of immiscible and miscible liquids at high pressures and temperatures. In this study, we have performed an X-ray radiography observation at a high pressure to precisely determine the immiscibility gaps of an Fe-O-S system at 3 GPa and a temperature of up to 2203 K.

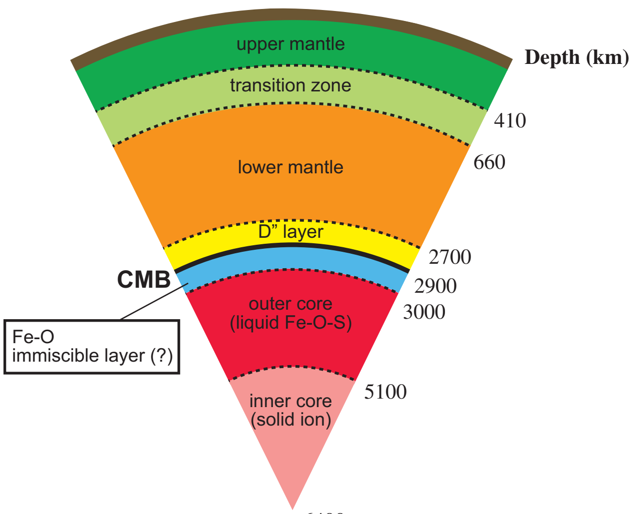

Fig. 1. The internal structure of the Earth. A 100 km layer underneath the core-mantle boundary (CMB) was suggested from a seismological observation [1].

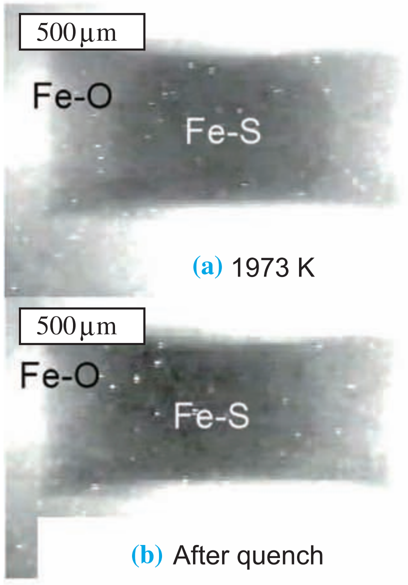

Fig. 2. X-ray radiographic images for a starting composition of $Fe_{65}O_{27}S_8$. **(a)** At 1973 K, Fe-S metallic liquid (dark gray) and Fe-O ionic liquid (light gray) were observed. **(b)** After quenching from 1973 K, two separated phases were observed.

Experiments were performed using an X-ray radiography technique, together with a 1500 ton Kawai-type multianvil apparatus (SPEED-1500) at beamline **BL04B1**. A transmitted X-ray from a sample is converted into visible light using a YAG scintillator and detected by a CCD camera. The starting materials were mixtures of Fe, FeS, and $Fe_{0.91}O$ powders with compositional ranges of 13-27% oxygen and 8-33% sulfur (in atomic ratio). A sintered Al_2O_3 capsule was used because it is less reactive with the samples than sintered MgO and hBN capsules, which are commonly used to study the reactions of liquid Fe with light element(s). Real time radiographic images were recorded as a digital file during heating and quenching. In this paper, we give the results of two representative experimental runs with starting compositions of $Fe_{65}O_{27}S_8$ and $Fe_{62}O_{23}S_{15}$ at 3 GPa.

Figure 2 shows the radiographic images for the starting composition of $Fe_{65}O_{27}S_8$. Immiscible liquids were observed at 1973 K, and two separated phases quenched from this temperature were observed. The dark and gray areas in Fig. 2 correspond to Fe-S metallic and Fe-O ionic liquids, respectively. This result shows that primary immiscible liquids can be quenched as two separated phases.

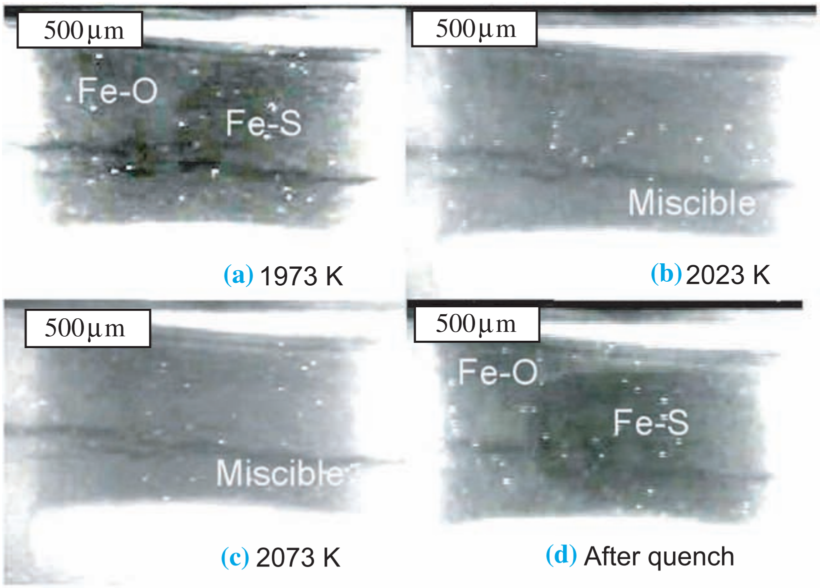

Fig. 3. X-ray radiographic images for a starting composition of $Fe_{62}O_{23}S_{15}$. **(a)** At 1973 K, Fe-S metallic liquid (dark gray) and Fe-O ionic liquid (light gray) were observed. **(b)** At 2023 K, a miscible liquid was observed. **(c)** At 2073 K. **(d)** After quenching from 2073 K, two separated phases that correspond to Fe-S metallic and Fe-O ionic compositions appeared.

Figure 3 shows the radiographic images for the starting composition of $Fe_{62}O_{23}S_{15}$. Immiscible liquids can be observed at 1973 K and these liquids became miscible at 2023 K (Fig. 3), indicating that the liquid miscibility gap closes between these temperatures. During quenching from 2073 K, the miscible liquid was suddenly separated into two phases (Fig. 3). This may be because the miscible liquid passed through the stability field of immiscible liquids during quenching.

Our results indicate that the two phases of the quenched products can be interpreted as either primary immiscible liquids or a single miscible liquid at high temperatures. Therefore, it is necessary to perform *in situ* observations to determine the precise liquid immiscibility gap. Both radiographic observations and the chemical analysis of samples from additional quenching experiments show that the liquid immiscibility gap decreases with increasing temperature at 3 GPa [5].

The light elements potentially in the Earth's core are not only oxygen and sulfur, but also silicon and carbon. In future, melting experiments in other systems, such as Fe-S-Si and Fe-S-C, will also be important for obtaining a better understanding the properties of the Earth's outer core and confirming the existence of the outermost layer in the outer core.

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