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Development of heavy mineral and heavy element database of soil sediments in Japan using synchrotron radiation X-ray powder diffraction and high-energy (116 keV) X-ray fluorescence analysis
1. Case study of Kofu and Chiba region

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ABSTRACT

We have started the construction of a nationwide forensic soil sediment database for Japan based on the heavy mineral and trace heavy element compositions of stream sediments collected at 3024 points all over Japan obtained by high-resolution synchrotron X-ray powder diffraction (SR-XRD) and high-energy synchrotron X-ray fluorescence analysis (HE-SR-XRF). In this study, the performance of both techniques was demonstrated by analyzing soil sediments from two different geological regions, the Kofu and Chiba regions in Kanto province, to construct database that can be applied in the future to provenance analysis of soil evidence from a crime scene. The sediments from the quaternary volcanic lithology of the Chiba region were found to be dominated by heavy minerals of volcanic origin – orthopyroxene, clinopyroxene, and amphibole, and the REEs (rare earth elements) within the region showed similar geochemical behavior. On the other hand, four distinct heavy mineral groups were identified in the sediments of the Kofu region, where there is a great variety of underlying bedrock, and the geochemical behavior of the REEs in the sediments also varied accordingly to their geological origins. As such, our study shows that high-resolution SR-XRD data can provide information on the spatial distribution patterns of heavy minerals in stream sediments, playing an important role in determining their likely geographical origin. Meanwhile, the highly sensitive HE-SR-XRF data allow us to study the geochemical behavior of trace heavy elements, especially the REEs in the sediments, providing additional support to further constrain the likely geographical origin of the sediments determined by heavy minerals.

1. Introduction

The analysis of earth-related materials (soils, sands, sediments) is a very important task for many forensic science laboratories, as the materials can provide important information to criminal investigations as transfer evidence [1]. Many criminal cases take place under circumstances such that earth-related material transfers to a criminal or victim's shirt, shoes, etc. Classically, the materials on a suspect's shoe might be compared with those collected from the scene of a crime, and a detailed study of the properties of the materials would indicate that the suspect had or had not been at the crime scene. In recent forensic examinations, earth-related materials have also been collected for the purpose of aiding in an investigation (i.e., identifying the provenance of soil sediment collected from a suspect's car in order to identify the scene of the crime) [2]. In such studies, earth scientists are often asked to establish or constrain the likely provenance of the material as part of the forensic investigation. Through analysis of the material, it may be possible to achieve the ultimate goal of naming the location or at least several likely ones, hence narrowing the investigation area. However, these investigations are typically more difficult than the comparative ones since the purpose is to describe an unknown location based only on the internal evidence that the earth-related material itself can provide. Without access to extensive databases on the properties of the materials, these investigations are difficult, and it is also a very challenging task for the analytical earth scientists to predict the origins of the materials. In this regard it will be very helpful if we have a set

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of database for comparison, and such a database could provide important clues in directing or aiding an active forensic investigation.

Sediment (soils or sands) mineralogy that differs sufficiently from different geological regions has long been used as a provenance indicator in forensic investigations [3]. Of particular interest are the proportions and characteristics of heavy minerals (e.g., amphibole, zircon, and orthopyroxene), which are the diagnostic indicators of sediment provenance in forensic investigation. Heavy minerals are here defined as mineral grains with a density higher than 2.85 g/cm^3. They are less present in most sediments than light minerals, particularly in sands, in a rather small proportion and show great diversity of mineral species (over 30 translucent detrital species of common occurrence) in different geology units [4]. Some minerals are characteristic of a particular kind of source rock – olivine, for example, is indicative of a mafic or ultramafic rock source [5,6]. These characteristics provide important petrological information for pinpointing the geological source to which the sand or soil is related, and make heavy minerals a very sensitive provenance indicator. Light minerals such as feldspar and quartz, which can commonly be found on the surface of the earth, are however, less diagnostic. Recently, heavy minerals have been utilized in a wide variety of forensic applications. Several case studies have been reported by Isphording [7] demonstrating how heavy minerals can be used in murder investigations, identification of the source of ground water contamination, industrial sabotage investigations, etc.

In addition, the provenance of forensic sediment samples can be further constrained if information regarding their geochemical heavy elements signature is obtained. These heavy elements are particularly useful in fingerprinting the geological origin of the samples. Such an approach has been successfully demonstrated by Nakai and his co-workers [8,9] who developed high-energy synchrotron radiation X-ray fluorescence (HE-SR-XRF) analysis utilizing 116 keV X-ray for discrimination of the trace heavy elements of arsenic acid from different sources in an arsenic curry murder case. In that case, they successfully characterized the arsenic acid from a selection of sources, including samples obtained from the curry and suspect's home based on their heavy element signature. This was the first application of synchrotron radiation X-ray analysis to solve a real crime.

In our ongoing research, our intent is to develop a nationwide heavy minerals and heavy elements database of stream sediments collected from all over Japan for forensic purposes based on the expectations of the National Police Agency of Japan. High-resolution synchrotron radiation X-ray diffraction (SR-XRD) analysis and HE-SR-XRF analysis utilizing high-energy X-rays of 116 keV were applied in this study. The sediment samples were supplied from the Institute of Geology and Geoinformation, AIST, which had been analyzed by ICP-AES/MS and AAS for a nationwide geochemical mapping program at a 1:2,000,000 scale in 1999 [10–12]. A total of 3024 stream sediments were collected across Japan at a sampling density of 1 site per 120 km^2. Since Japan is a relatively small landmass with a great variety of parent rocks, it is likely to be well-suited to the application of these approaches. We believe that by comparing the forensic materials with both the heavy minerals and heavy trace elements databases, it will be possible to identify the potential source areas of the materials, which in turn will provide clues in aiding and/or directing active forensic investigations. Therefore, this study is intended (1) to describe and evaluate the performance of two synchrotron techniques that were developed to perform the examinations on the sediment samples, and (2) to demonstrate the potential of databases that could be used in forensic investigation by interpreting the heavy minerals and trace heavy elements data collected from the Kofu and Chiba regions in Kanto province of Japan.

2. Background for the SR analytical techniques

In recent years, synchrotron radiation that produces high-brilliance, high-coherence X-rays offers a superior light source for many X-ray analytical techniques, e.g. X-ray fluorescence, X-ray diffraction, and X-ray absorption fine structure analysis (XAFS), that could play a major role in forensic trace evidence analysis [8,9,13–16]. The brightness of the photon beam of synchrotron radiation can be several orders of magnitude greater than any conventional laboratory X-ray sources. Coupled with the high performance of andulators and wiggler insertion devices, highly brilliant monochromatic X-rays can be selected at the experimental beam line, providing great improvements in energy resolution ($\Delta E/E$) with enhanced signal-to noise-ratios [17].

Although XRD is a proven technique for mineral identification and is routinely used in forensic laboratories for the characterization of mixed phases in geological materials, the sensitivity and resolution of the conventional laboratory instrument are quite limited and data collection can be time-consuming due to the limited intensity of X-ray sources. Hence, the diffraction patterns obtained usually reveal dominant mineral components, while minor phases such as heavy minerals are generally at the level of background noise or are unresolved from overlapping dominant reflections. In the present study, an SR-XRD technique that significantly benefited from specific features of synchrotron radiation (high brilliance, high energy, and high coherence) was used to analyze the heavy mineral compositions of the sediments. The SR-XRD measurement system can provide high-resolution data; the diffraction line width (FWHM) of the 111 reflection peak of the standard sample, CeO_2 is ca. 0.04° 2θ degrees, which is significantly narrower than that measured by conventional laboratory X-ray diffractometer. This high-resolution SR-XRD data have greatly increased our ability to identify complex mixtures of mineral phases in the sediment samples.

On the other hand, chemical analysis of small amounts of sediments is generally carried out by electron microprobe (EPMA) or scanning electron microscopy with an energy-dispersive X-ray spectrometer (SEM–EDS) and ICP-MS/AES in most forensic laboratories. The detection limit of EPMA/SEM–EDS is poor, typically at 0.01 wt%, and the sensitivity is particularly insufficient for trace heavy elements analysis [16]. Conventional SEM–EDS analyses are usually carried out using characteristic X-rays with energy less than 20 keV. In this energy range, the L emission lines of the trace heavy elements usually severely overlap with the crowded K, L, and M emission lines of the major component elements, causing difficulties in either qualitative or quantitative study of the heavy elements. This overlapping problem was solved with HE-SR-XRF analysis utilizing X-rays of 116 keV [9,18]. The high-energy X-rays (116 keV) from the third-generation SR Wiggler sources of SPring-8 is able to excite the K-series lines of trace heavy elements, including Uranium [18]. Such X-rays enable us to analyze the trace heavy elements at the ppm level from trace amounts of sediment samples by using their K emission lines. HE-SR-XRF is suitable to obtain the bulk trace heavy element composition because of the high transmission power of the high-energy X-ray. Compared to highly sensitive ICP-MS/AES techniques, HE-SR-XRF offers the benefit of simple and nondestructive sample preparation.

Although synchrotron radiation sources have proven to be highly beneficial in many research fields for the characterization of forensic materials, as demonstrated by a number of workers worldwide [8,13–16,19,20], only a very limited number of studies have been conducted in this field of research. This lack of research is due to access to synchrotron facilities being somewhat limited, making them not necessarily available for routine analysis. Other than that, the instrumental setting at the experimental hutch