Spectroscopic Studies of Mössbauer, Infrared, and Laser-Induced Luminescence for Classifying Rare-Earth Minerals Enriched in Iron-Rich Deposits

Noboru Aoyagi,* Thuy T. Nguyen, Yuta Kumagai, Tung V. Nguyen, Masami Nakada, Yukari Segawa, Hung T. Nguyen, and Thuan Ba Le

ABSTRACT: Rare-earth (RE) phosphates often appear as an accessory phase in igneous or metamorphic rocks; however, these rocks are composed of myriad chemical elements and nuclides that interfere with the qualitative or quantitative analyses of the RE phosphates over a range of concentrations in the absence of a pretreatment. In addition, the limit of each analytical methodology constrains the approach as well as the usefulness of the results in geoscience applications. Here, we report the specific mineral characterization of RE-containing ores from Yen Phu mine, Vietnam, using a range of state-of-the-art spectroscopic techniques in conjunction with microscopy: Mössbauer spectroscopy, infrared microspectroscopy, time-resolved laser-induced fluorescence spectroscopy (TRLFS), and scanning electron microscopy with energy-dispersive X-ray spectroscopy. Because the distribution of each element in the deposit differs, such combinatorial works are necessary and could lead to more plausible answers to questions surrounding the point of origin of RE elements. The results of our Mössbauer spectroscopic analysis indicate that the three ores sampled at different locations all contain magnetite-like, hematite-like, and iron(III) salts other than hematite. In addition, we confirmed the presence of phosphate around the grain boundary in the magnetite-like mineral phase by infrared microspectroscopic analysis. The present analytical findings of trace amounts of europium(III) using TRLFS suggest that the europium ions generate identical luminescence spectra despite being embedded in three different matrices of iron minerals. This demonstration highlights the benefits of combinatorial spectroscopic analyses to gain insights into the effects of the environment of REs on their solid-state chemistry and shows the potential utility of TRLFS as a resource mining tool. Further applications of this approach in the analytical screening of rocks and minerals are feasible.

INTRODUCTION

The magmatic assimilation giving rise to the incorporation of rare-earth elements (REEs) into igneous rocks on the surface of the Earth’s crust is a fundamental aspect of understanding the origin of REE-containing rocks and minerals. These (most typically, monazite and xenotime) are the REE−orthophosphate minerals found as accessory phases of rocks such as gneisses, granitoids, pegmatites, and rhyolites. Among other techniques, microscopy and powder X-ray diffraction (PXRD) are indispensable for determining mineral phases not only in mineralogy or geochronology but also in resource geology as tools for basic characterization. Such analyses are important because these geochemical findings provide us with the prehistory of rocks. For example, the monazite phase can coexist with the xenotime phase in many igneous or metamorphic rocks depending on the temperature and pressure conditions at their primeval time. Such geological history can be termed “thermometry” to calibrate the miscibility gap in the series of the CePO₄−YPO₄ binary system. REEs are, on average, relatively abundant in the Earth’s crust but are generally not sufficiently concentrated for them to be easily exploitable commercially. In particular, three typical mineral resources to mine are bastnaesite (Ce, La) CO₃F, monazite (La, Ce, Nd) PO₄, and xenotime YPO₄. Among these minerals, REE−orthophosphate minerals such as monazite and xenotime occur together in many rocks. They are commonly accompanied by heavy REEs (HREEs) as accessory elements in both igneous and metamorphic rocks. However, they exhibit different properties depending on the preference of REEs upon incorporation: monazite preferentially uptakes light REEs (LREEs), whereas xenotime preferentially uptakes HREEs. 

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Although the single-crystal structures of natural or synthetic monazite and xenotime have been researched intensively in laboratory settings, their native compositions that include various components or trace amounts of impurities, their intermingled lattice structures, and their origin in nature have not been fully established because of the complexity stemming from their chemical heterogeneity upon forming a solid solution. Hitherto, the cutoff quality of the mineral resources to mine is not as high as it used to be. Therefore, a technical challenge in the determination of the chemical state of REEs in these host matrices is the in situ screening of native ores at a trace level in the presence of interfering impurities.

Here, we present a strategy of applying spectroscopic techniques to crudely classify the chemical environment of REEs in different rocks: deposits in Vietnam were selected for a specific test case because they contain a large amount of iron as an impurity. Because iron minerals are ubiquitous in igneous rocks, the accessory RE minerals are often associated with iron host rocks, especially in sediments.4−11 However, because of their relatively large ionic radii, REEs are not generally considered to incorporate into the major rock-forming minerals such as olivine, pyroxene, feldspar, or magnetite. These facts appear to be contradictory. Therefore, an in-depth understanding of the interaction of REEs with an iron matrix is a key issue for the mineralogical classification during surveys in future resource mining.

To examine whether a correlation exists between REEs and host matrices, we conducted elemental analyses of REEs and iron, both of which form oxides as impurities in inhomogeneous phosphate rocks. The detailed identification of the iron minerals was carried out using Mössbauer spectroscopy as well as PXRD. Despite the chemical information about igneous or metamorphic rocks, less attention has been paid to whether organic anions could be decomposed at elevated temperature to form igneous rocks. We emphasize the infrared (IR) microscopic analysis of anions forming iron-rich ores because the chemical surroundings and corresponding symmetry around REEs strongly influence their electronic spectra. We also use laser spectroscopy to study the chemical environment of REEs in iron oxide minerals in depth. Furthermore, theoretical considerations in interpreting the spectral shapes are based on recent applications of the modified Judd−Ofelt (J−O) theory. We compare the spectroscopic trends with the results of chemical analyses conducted by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM−EDX) and inductively coupled plasma optical emission spectrometry (ICP−OES). On the basis of the spectroscopic analysis results, we propose that such combinatorial analyses are applicable not only in analytical investigations of chemical composition but also for determining chemical states—where they are plausibly helpful in elucidating the history of migration of REEs in metamorphic rocks.

■ RESULTS AND DISCUSSION

Basic Characterization by Microscopy and X-ray Diffraction. A total of three deposits were investigated in this study. Three different ores corrected at the same geological site—magnetite-like ore (a), hematite-like ore (b), and mixture ore (c)—were investigated by microscopic methods (Figure 1a) because the iron mineral phases among these ores differed, as characterized vide infra. The results of surface analyses at the intersections of the specimens by polarized optical microscopy (POM) (crossed Nicole by reflection) and SEM−EDX are shown in Figure 1. We found that Si and Fe are enriched in different domains, whereas REEs such as La, Ce, Pr, and Nd are concentrated on identical domains as Fe but with different EDX spectral intensities. This observation clearly indicates that the REEs are stable within the iron mineral phases. Similar trends were observed for ores (a) and (c) (results not shown); on the contrary, ore (b) was not followed by the trend. The iron oxides are plausibly associated with that of the REEs on the basis of charge neutrality in the bulk mineral. The REEs La, Pr, and Nd are generally trivalent ions in the solid state, whereas Ce is typically tetravalent. Thus, on the basis of this observation, the iron in the minerals could be assigned as mainly trivalent, that is, Fe\textsubscript{III}\textsubscript{O}\textsubscript{3} (hematite). Lighter elements such as Ca and P are also shown in Figure 1. Ca did not appear in this area of interest; however, we found two domains rich in P, implying the existence of apate-related rocks.

To the best of our knowledge, the incorporation of REEs into igneous and metamorphic rocks composed of iron-related minerals is well-known. The identification of mineral phases is necessary to determine which minerals are accompanied by iron materials in the deposit. The PXRD patterns in Figure 2 reveal that at least three typical iron phases are involved: hematite, magnetite (Fe\textsubscript{III}(Fe\textsuperscript{II}, Fe\textsubscript{III})O\textsubscript{4}), and other salts of Fe\textsubscript{III}. Here, powders of ores (a), (b), and (c) were prepared by grinding the ores. The PXRD patterns of these three samples indicate the presence of uniformly dispersed hematite and magnetite. In particular, hematite-like peaks are predominantly present in the pattern of ore (a) at 2θ = 21, 33, and 50°, accompanied by a remarkable peak of quartz at 2θ = 26°. A small peak at 2θ = 24° is also present; we attributed this peak to FePO\textsubscript{4} in the hematite-like matrix. This peak was not detected in either the pattern of ore (b) or that of ore (c).12,13 In addition, the pattern of ore (b) shows that it is composed of a mixture of hematite-like minerals and magnetite-like minerals. By contrast, the pattern of ore (c) shows that a magnetite-like phase was predominant. Because of the grade of the REEs in the corresponding ores—the total RE oxide (TREO) content is approximately 2% at the highest estimation, indicating that the content of each REE component is less than 0.1%—the presence of RE phosphates such as...
Figure 2. Images and PXRD patterns of REE ores (a–c). Reference patterns of hematite and magnetite are cited from the literature.15,16 Sources: (Magnetite) adapted from Glazyrin, K.; McCammon, C.; Dubrovinsky, L.; Merlini, M.; Schollenbruch, K.; Woodland, A.; Hanfland, M. Effect of high pressure on the crystal structure and electronic properties of magnetite below 25 GPa. Am. Mineral. 2012, 97, 128-133. Copyright 2012 Mineralogical Society of America; (Hematite) adapted from Duttine, M.; Dambournet, D.; Penin, N.; Carlier, D.; Bourgeois, L.; Wattiaux, A.; Chapman, K. W.; Chupas, P. J.; Groult, H.; Durand, E.; Demourgues, A., Tailoring the Composition of a Mixed Anion Iron-Based Fluoride Compound: Evidence for Anionic Vacancy and Electrochemical Performance in Lithium Cells. Chemistry of Materials 2014, 26, 4190-4199. Copyright 2014 American Chemical Society.

Figure 3. Mössbauer spectra of powdered ores (a–c). Black dotted lines are the data. Peak deconvolution depicts three iron phases: magnetite (blue), hematite (red), and FeIII salt (green).

xenotime or monazite was not confirmed by the results of the present screening test for powder materials.17,18

Mössbauer Spectroscopy and IR Microspectroscopy for the Determination of Iron Phases. Although the SEM and PXRD results provide chemical composition and crystal information, they do not clarify the roles of minor components. Therefore, we used Mössbauer spectroscopy (Figure 3) to analyze these iron-based minerals to identify the minerals as well as the oxidation states of iron in the minor components; the results were confirmed by micro-IR spectroscopy analysis (Figure 4). The results for ore (a) in Figure 3 explicitly indicate the presence of FeIII ions forming a salt; the doublet peak at approximately 0.3 mm/s (green line) implies that FePO4 is the dominant phase, with an approximately equivalent mixture of hematite and magnetite forming the reccessive phase. By contrast, ore (c) is a mixture of FeII salts and magnetite; hematite is not predominant. Interestingly, the spectrum of ore (b) indicates that these three Fe phases coexist in this ore. This finding is consistent with the interpretation of the multiple peaks in the PXRD patterns. The sensitivity of detection of each Fe phase, however, differs between the PXRD and Mössbauer methods. Thus, we cannot quantitatively compare the FeII salt and magnetite contents using these techniques. These results both suggest, however, that at least two or three Fe phases coexist in ores (a–c).

The global composition and fraction of the REOs (see also Table 1) were analyzed, and the results show that FeIII ions are very rich. One possible hypothesis is that the REIII atom is uptaken into the host matrices of Fe-related minerals. Nevertheless, the chemical species of the FeIII ions remains elusive; that is, the question of which surrounding donor atoms or molecules are favored or feasible remains unanswered.

To answer the aforementioned question, micro-IR spectroscopy would be a powerful technique because it can indicate the existence of molecular ligands that coexist upon the surface of the solid.17,18 Most interestingly, we observed two peaks assigned as P–O vibration modes, which indicate that phosphate groups are embedded in the area of interest indicated as spot (i) in Figure 4a. Symmetrical stretching vibrations of a P–O bond were observed at 1078 and 1211 cm−1, whereas asymmetrical stretching of a P–O bond was observed at 1267 cm−1 in the spectrum corresponding to spot (i). In the spectrum corresponding to spot (iii), a weak band associated with P–O–P appears at 795 cm−1 and a Si–O stretching vibration appears at approximately 879 cm−1. Given that Si and Fe were observed in different domains in Figure 1c, the present observations by IR microscopy indicate that the uptake of the phosphate anions could occur in the presence of a metal center such as FeIII or REIII. This interpretation is consistent with the distribution observed in the SEM–EDX elemental mapping images (vide supra); phosphorus is associated with Fe and REE ions. By contrast, the peaks due to the presence of carbonate ions are weak, indicating that carbonate ions are less abundant than phosphate ions (Figure 4b).

Laser-Induced Luminescence Spectroscopy for the Evaluation of EuIII Coordination Geometry in the REE–Phosphate Deposits. The results, which indicate that REEIII ions occupy FeII sites and are accompanied by phosphate anions, provide information about the in situ chemical environment of the REEs in this iron-rich deposit—specifically, that REEIII(PO4) exists. The direct observation of this chemical species is technically challenging because of the low sensitivity stemming from the high concentrations of Fe, silica, or other light metals as well as the poor selectivity in minerals. Hence, we used laser-induced luminescence spectroscopy to achieve an in-depth understanding of the chemical speciation of REEs in the present series of deposits. Detailed
information about the principles of this technique is described elsewhere.19,20 Moreover, the centrosymmetric structure around REE ions has often been investigated by fluorescence spectroscopy.21,22 Because of its intense emission, we selected the EuIII ion as an effective indicator to characterize the centrosymmetric geometry around EuIII as a chemical homologue of the other REEs. The comprehensive spectrum in Figure 5 shows the luminescence spectra of several REEs, recorded with a set of different excitation wavelengths: 350, 365, and 395 nm. These emission bands are attributed to TbIII ions at ∼550 nm and EuIII ions at 585–615 nm. The well-known peak in the absorbance spectrum of Eu3+ in solid materials appears as the 4f−4f transition, typically at approximately 394–395 nm (5L6 ← 7F0). Furthermore, the time-resolved laser-induced fluorescence spectroscopy (TRLFS) results for the reference samples—Eu(PO4), Eu2(CO3)2, and Eu2O3—are shown in Figure 5b, where the spectral intensity of Eu(PO4) at ΔJ = 1 (∼592 nm) is different from those of Eu2(CO3)3 and Eu2O3.

The luminescence spectra of Eu3+ in Yen Phu ores (a), (b), and (c) are also compared in Figure 6. The peak I2 (ΔJ = 2, ∼617 nm) becomes hypersensitive through the series,

| Table 1. Major Elements and REEs in the Yen Phu Concentrate (%) and REEs in the Yen Phu Ore (in mg/kg). Concentration Determined by ICP–OES |
| --- |
| **Elements** | **Concentration** | **Elements** | **Concentration** |
| **Si** | 16.177 | **Y** | 5.37 |
| **Fe** | 16.4 | **La** | 1.41 |
| **Al** | 1.08 | **Ce** | 32.85 |
| **Ca** | 1.03 | **Pr** | 0.2 |
| **P** | 43.95 | **Nd** | 32.72 |
| **K** | 0.14 | **Sm** | 0.53 |
| **Na** | 0.07 | **Eu** | 0.06 |
| **Ti** | 0.15 | **Gd** | 0.65 |
| **Mn** | 0.16 | **Tb** | 0.04 |
| **Cr** | 0.01 | **Dy** | 0.87 |
| **Ba** | 0.17 | **Ho** | 0.19 |
| **Cu** | 0.03 | **Er** | 0.77 |
| **Nb** | 0.05 | **Tm** | 0.06 |
| **Th** | 0.166 | **Yb** | 0.43 |
| **U** | 0.044 | **Lu** | 0.06 |
| **Total** | 27.01 | **Total** | 16.2 % TREO |

Figure 4. Integrated image of micro-IR spectroscopy (a), extended spectra of (i–iv) REE ore c at higher wavenumber (b), and raw spectra of (i–iv) corresponding to the REE ore c at lower wavenumber (c).

Figure 5. Photoluminescence spectra of the untreated Yen Phu RE ores (a) and reference powder samples (b).

Figure 6. Photoluminescence spectra of Yen Phu powdered ore samples (a–c) excited at a series of different wavelengths.
changing the ratio $R_{12} \equiv I_2(\Delta J = 2)/I_2(\Delta J = 1)$ within a certain range ($4.67 - 4.88$), as listed in Table 2. This ratio was also investigated for ores with different origins for reference, as shown in Table 3. The first value in the table (4.76(31)) indicates the mean value from Table 2, and the standard deviation is given in parentheses. This $R_{12}$ differs substantially from those obtained for the Dong Pao ore (2.67(23)) and monazite ore (2.48(16)). With respect to the spectral shape, especially around the $I_2$ ($\Delta J = 2$) peak, the shoulders at ~612 nm differ among these ores.

To extend the usefulness of luminescence spectroscopy for classifying general RE deposits, we also evaluated the $R_{12}$ peak ratio for the ores of different origins (Table 3) on the basis of their spectra in Figure 7; however, the REE concentrations in the Dong Pao samples and the monazite ore were insufficient. These results reveal a drawback of applying luminescence spectroscopy for resource mining in that weak signals may be obtained because of poor quality ores or quenching effects. Furthermore, quenching can occur either when a strong quencher is present or as a result of self-quenching because of an excessively high-quality ore. For example, Fe ions have a strong luminescence quenching effect in solutions.23 Further investigations of the extended utility of luminescence are necessary.

To better understand the effect of the chemical environment on luminescent properties of Eu$^{3+}$ ions in a pure host matrix, the standard J–O theory is helpful, especially for interpreting REE$^{3+}$ electronic spectra and estimating the transition probability of 4f electrons.24 In their conclusive formulation, the general expression becomes

$$S_{\text{f-r}} = \sum_{\lambda=2,4,6} \Omega_{\lambda}^2 | \langle \Psi_{\lambda} | U^{(\gamma)} | \Psi_{\Omega} \rangle |^2$$

where $S_{\text{f-r}}$ denotes intensity and $\Omega_{\lambda}$ ($\lambda = 2, 4, 6$) are the J–O parameters. These $\Omega_{\lambda}$ values include the angular terms, radial integrals, and coefficients of coupling and recoupling of the angular momenta; the energy states are included within the reduced matrix element, $U^{(\gamma)}$, of the unit tensor operator; the wavefunctions $\Psi_{\lambda}$ and $\Psi_{\Omega}$ represent the initial state and the final state, respectively. With an increasing number of investigations, theoretical and experimental interpretations using the J–O theory continue to improve.25-28 Tutorials and practical reviews are also available.29 In particular, Ciric et al.30 recently developed application software to calculate the J–O parameters, which introduces the possibility of numerous experimental works on Eu$^{3+}$ similar to the approach used in the present study. Despite the tremendous efforts invested in these benchmark studies, their applicability in the present case is limited because of the heterogeneity of our samples. Information about the refractive index, crystal field, and luminescence lifetime is necessary to obtain the $\Omega_{\lambda}$ values. Indeed, some of these inputs could be estimated for the calculation of $\Omega_{\lambda}$ for our ore samples; however, we could not evaluate the luminescence lifetimes for all of the samples because of the weak luminescence signals. We therefore instead refocus on the peak ratio $R_{12}$ as an indicator of a mixture of natural minerals. To date, numerous chemists have supported the hypothesis that the centrosymmetric structure around RE$^{3+}$ ions affects the spectral shape as well as the $\Delta J/\Delta J_{\text{J-O}}$ ratio. However, as noted in criticisms in the literature, drawing conclusions from structural analyses based only on luminescence spectra is inappropriate.23 Accordingly, we carried out combinatorial spectroscopy to apply this index as a complementary finding.

**General Discussion of the Implications for REE Resource Mining.** REEs appear to be enriched with RE ions that substitute for Fe atoms in mixtures of iron oxides and iron phosphates in the subsurface of the lithosphere. The implications of this finding differ from those of previous works that claim that the enrichment of REEs is mainly associated with adsorption onto kaolinite and its related minerals in weathered crust.30 For example, Fe–Mn oxides (i.e., deep-sea ferromanganese) are well known to enrich REEs.31 In the Fe–Mn oxides, Mn plays a more important role than Fe. Moreover, in other cases, sedimentary or metamorphic rocks accommodate REEs. In the sedimentary or metamorphic rocks, REEs

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**Table 2. Peak Ratios Obtained from TRLFS**

| sample                  | $R_{12}$ |
|-------------------------|----------|
| ore a                   | 4.9      |
| ore b                   | 4.7      |
| ore c                   | 4.7      |

**Table 3. Peak Ratios Obtained from TRLFS**

| materials                                      | $R_{12}$ |
|------------------------------------------------|----------|
| Yen Phu ore avg                               | 4.7(3)   |
| Dong Pao ore                                  | 2.7(2)   |
| Seashore monazite ore (ilmenite processing)   | 2.5(2)   |
| Eu(PO$_4$)$_3$                                | 1.2      |
| Eu$_2$(CO$_3$)$_3$                            | 4.2      |
| Eu$_2$O$_3$                                   | 4.8      |

**Figure 7.** Photoluminescence spectra (77 K) of powdered ore samples at different origins: (a) Yen Phu, (b) Dong Pao, and (c) seashore.
form orthoferrite (REE) FeO3 compounds. On the contrary, our findings from our analysis of the Yen Phu ore, which is a mixture of igneous rocks and metamorphic rocks, imply that iron phosphate minerals play an important role in the enrichment of REEs. This finding is explained by light elements such as P, K, and Ca being less sensitive and preliminarily found to be less abundant in RE concentrates, as investigated by ICP–OES (vide infra); in addition, the multiple P–O stretching vibrations observed in the micro-spectra indicate that P–O or REE····O–PO3 bonds are assignable to the Fe-rich surface. In Figure 4, two peaks corresponding to the noncoordinated mode of a metal center (the P≡O stretching) appear at 1211 (i) and 1213 cm−1 (iv) (differences of 33 and 35 cm−1 from 1178 cm−1, respectively). These bands are also among the bands commonly observed in the spectra of REEs other than those containing Eu or Tb ions.

We could determine the predominant crystalline phase from the series of XRD patterns; however, the detailed chemical environment around the REEs had yet to be obtained because of the limited sensitivity of XRD to trace metals. Yet, the complementary or rather principal measurement by Mössbauer spectroscopy revealed that Yen Phu minerals have mainly two different iron oxide minerals (maghemite and hematite) with a small amount of iron phosphate. The phosphate ligand has a high affinity to REE ions as well as to Fe ions; the equilibrium reaction is competitive in solutions. In addition, the phosphate anion has several different forms available to coordinate with. Therefore, the challenge in luminescence spectroscopy is to selectively assign spectral features to metals on the basis of their energy levels. The results indicate that peaks associated with Tb, Eu, and other metals occur simultaneously (Figure 5a): a peak at 548 nm in the series of the luminescence spectra correspond to the transition 5D4 → 7F3 for the Tb3+ ion, is dependent upon the excitation wavelength because the oscillator strength changes in UV-light absorption. Multiple non-negligible peaks of Eu3+ ions also appear (7D0 → 7F2 (≡ΔJ1, at ∼590 nm), 7D0 → 7F1 (≡ΔJ2, at ∼620 nm), and 7D0 → 7F3 (≡ΔJ3, at ∼700 nm)), and their shapes are also dependent upon the excitation wavelength. Nevertheless, another possibility exists for forming REO3 in the iron oxide phases; this oxide is the most plausible form, and the spectral shapes are found in the literature datum. Hence, we measured pristine samples of commercially available Eu(PO4)2, synthesized Eu2(CO3)3, and Eu2O3 as reference luminescence spectra (Figure 5b). Fortunately, the spectrum in Figure 5a corresponding to the Yen Phu ore (a) with excitation at λex = 395 nm and the spectrum of Eu(PO4)2 are almost identical in shapes. 1.0 ≤ R12 (≡I1(ΔJ = 2)/I1(ΔJ = 1)) ≤ 1.2. However, whether these spectra match remains an open question because of the low signal-to-noise ratio in Figure 5a and the inconsistent spectral shape in Figure 6. Thus, we propose that these REEs are bound to the phosphate anion. Otherwise, the most likely state for Eu would be the oxide, Eu2O3, indicating that other spectroscopic methods should be applied. Nonetheless, choosing which chemical species of EuIII (i.e., Eu(PO4)2, Eu(CO3)3F, or Eu2O3) is preferable in the iron oxides investigated in the present work is challenging because of the spectral shape, particularly the R12 value for the reference samples in Table 3 is rather closer to those of Eu2(CO3)3 or Eu2O3 (Table 3). Interestingly, the R12 ratio of Eu2O3 (4.76) is identical to that of the Yen Phu ore; however, we have not evaluated the accuracy and intrinsic errors in these measurements. Given that the amount of CO32− anions is negligibly small, as determined from the IR spectra (Figure 4b), we reasonably speculate that Eu2O3 is the chemical structure found by TRLFS, although the details have yet to be analyzed. However, this question is plausibly answered by the quantum yield of fluorescence of carbonate species and oxide species being higher than that of phosphate species. Our microspectroscopy results identify very weak carbonate moieties (at ca. 1500 cm−1) as well as phosphate species, which are predominant. Therefore, the ore investigated is composed of a mixture of dominant Eu(PO4)2 and ultratrace amounts of Eu–CO3-related compounds. The optimization of the laser setup using a cryostat (<10 K) would improve the quantum efficiency to enable this method to be extensively used in source mining surveys to identify potential RE deposits.

**CONCLUSIONS**

We demonstrated the spectroscopic characterization of REE-containing ores sampled from both the northwest and south seashore of Vietnam. The LREEs—La, Ce, Nd, and Pr—are accompanied by iron in the corresponding domains. The middle REEs (MREEs)—Eu and Tb—were also confirmed in the bulk analysis. The HREEs—Dy and Tb—were also present in concentrations below the lower detection limit of laser spectroscopy in the present study. This strong correlation of the presence of REEs with iron implies that these trivalent metal elements migrate or chemically exchange during the formation of rocks. Evidence of this phenomenon has also been found in sediments, as reported in a recent paper. Therefore, we examined the oxidation state of iron using Mössbauer spectrometry; the presence of three iron phases—maghemite, hematite, and iron(III) salts—was confirmed. Furthermore, the iron(III) phase was observed in detail using IR microspectroscopy, and we found that phosphate anions were distributed on the surface of the iron materials. The incorporation of Eu(PO4)2 into iron oxides or iron phosphates in the presence of Eu2O3 as well as Eu–CO3-related compounds was confirmed through combinatorial spectroscopy methods. Finally, photoluminescence spectra of MREEs Eu and Tb in trace amounts were recorded. We classified the symmetry in the EuIII luminescence spectra on the basis of the peak ratio analysis. The coordination geometry of these metals in the host matrices of the iron phase has yet to be determined. However, on the basis of the present findings, a more statistically established study would be preferable as a screening survey for the amount of REEs; in addition, the analysis of coexisting molecules would also be beneficial in analyzing the chemical state of REEs in the deposits.

**MATERIALS AND METHODS**

**Geology and Sample Materials.** We selected various sample ores from three different deposits across Vietnam: Dong Pao mine, Yen Phu mine, and Binh Thuan Province. Details of these areas have been reported elsewhere. Briefly, the geology is overviewed as follows. The Day Nui Con Voi (DNCV) massif bears a record of the Red River shear zone (RRSZ) activity located from South China to North Vietnam (Figure 1: MAP). A vast number of studies have been reported on the tectonic descriptions, geochronologic history, and the structure of the DNCV massif and its surrounding Triassic nappes: the metamorphic zone is chiefly formed with gneiss,
mica schists, and amphibolites.\textsuperscript{34,36,38,39} Although the DNCV massif has been referred to as carbonatite in the literature, the carbonatite mineralogy has not been fully described. Although the DNCV massif in China has been well reviewed, fewer studies in Vietnam have been reported.\textsuperscript{40} Because carbonatite prevails over the northernmost through the southernmost DNCV massif, we shall revisit its significance from the viewpoint of mineralogy using a spectroscopic approach in this paper.

These RE mineral deposits in North Vietnam—Dong Pao, Nam Xe, Yen Phu, and Muong Hum—are rich in economical RE metals. Among these deposits, those located at Dong Pao (bastnaesite) and Yen Phu (xenotime) are, in particular, known to accommodate large amounts of REEs.\textsuperscript{31} We paid particular attention to exploring the mineral composition of the RE deposit ores found at Yen Phu because of geological interest and because these ores are a potential resource for the future mining of REEs. Because some literature on the Dong Pao mine is available elsewhere, the Yen Phu RE deposit is described briefly here. The Yen Phu mine is located in the Yen Phu village, Van Yen district, Yan Bai Province, with geographical coordinates of 21°19' North latitude and 104°39' South longitude, approximately 200 km from Hanoi (Figure 8: MAP). The Ngoi Thia stream flows nearby and surrounds approximately one-half of the mine; it turns into a tributary of the Red River. The area is the southern vicinity of the DNCV fault, where the carbonatite is classified as a mixture of calcite, dolomite, and so forth. The carbonatite mineralogy includes apatite, monazite, magnetite, and hematite; however, the geological characterization of the Yen Phu mine comprises conglomerates and siltstones in detail as described in the literature.\textsuperscript{30} The deposit ores were sampled approximately 70 m from the surface as part of a previous research project; the ores are composed of the corresponding conglomerates and siltstones on the surface of the ground. The elemental analysis results for the typical xenotime and the corresponding RE concentrate obtained from the deposit are listed in Table 1. The procedure used to convert the seashore ore into a sample was a common ilmenite processing. In our preliminary work, XRD and ICP–OES analyses revealed that the majority forms of the minerals commonly found in the carbonatite were quartz (SiO\textsubscript{2}), goethite (FeO(OH)), kaolinite (Al\textsubscript{2}(Si\textsubscript{2}O\textsubscript{5})(OH)\textsubscript{4}), gibbsite (Al(OH)\textsubscript{3}), calcite (CaCO\textsubscript{3}), talc (Mg\textsubscript{6}(OH)\textsubscript{2}Si\textsubscript{3}O\textsubscript{10}(OH)\textsubscript{2}), and illite (K(Al\textsubscript{3}Fe\textsubscript{2})\textsubscript{0}Si\textsubscript{6}O\textsubscript{20}(OH)\textsubscript{2}H\textsubscript{2}O). Here again, we emphasize that the TREOs in the ore were at most 1.15%; our challenge was to detect REEs in the presence of massive impurities, where each REE exists at a trace level.

The main non-REEs in the Yen Phu concentrates were Si (16.67%), Fe (16.4%), P (3.95%), and Al (1.08%). The complementary example is also listed in Table 1. In addition, the Yen Phu xenotime concentrate contained high amount of REEs: the total content of REEs was \textasciitilde16.2 mass % Y and LREEs such as La, Ce, Pr, and Nd as well as MREEs Sm, Gd, and Dy. The Fe content of the ores was especially large; thus, a beneficiation process of REE concentrates would require the highly efficient removal of Fe impurities.

\textbf{Mössbauer Spectroscopy.}\textsuperscript{42} We determined the Fe(II)-to-Fe(III) ratios in the powdered ore samples by Mössbauer spectrometry. The Mössbauer spectrometer, a Laboratory Equipment VT-6000 equipped with a $^{57}$Co(Rh) source, was operated using constant acceleration motion. The Mössbauer spectra were obtained in the transmission geometry at room temperature. Initially, we calibrated the Doppler velocity using $\alpha$-Fe. The number of stacked thin sections varied depending on the relative intensity of absorption. We subsequently deconvoluted each Mössbauer spectrum by profile fitting with a set of Lorentzian functions. As a result, we found signals associated with only two iron oxidation states, Fe(II) and Fe(III), in all of the spectra. The Mössbauer spectra for the REE ore samples, along with their deconvoluted Fe(II) and Fe(III) profiles, are shown in Figure 3. Thus, the Fe(II)-to-Fe(III) molar ratios of were estimated from the intensities obtained from deconvoluted profiles ascribed to the two respective ions.

\textbf{Samples Preparation and Characterization by PXRD and SEM–EDX.} We identified the phases in the solid samples by PXRD analysis of the cross sections using Ni-filtered Cu K\textalpha radiation (D8 ADVANCE, Bruker). The ore specimens were then embedded in an acrylic resin. The surface of the cross section was polished using abrasive papers and then finish-polished with diamond paste. We observed the polished cross sections using a polarized optical microscope at room temperature and a scanning electron microscope; additionally, we analyzed the elemental composition in each phase using an EDS system (INCAPentaFETx3, Oxford Instruments) attached to the scanning electron microscope (VE-8800, Keyence). The polished surface of the sample was coated with carbon to avoid electrical charging; the details are available elsewhere.\textsuperscript{35,44} Table 1 shows the summary of the composition of the investigated ores.

\textbf{IR Microscopy.} We used the same specimen prepared for POM and SEM–EDX as the specimen for IR microscopy analysis (IRT-5200, Jasco) in conjunction with Fourier transform IR spectroscopy (FT-IR) (FT-IR 6100, Jasco); we used this apparatus to obtain images and FT-IR spectra, respectively. A standard mid-band MCT detector was used. As a reference material to calculate reflectance, the surface of the samples was coated with Au.

\textbf{Laser-Induced Fluorescence Spectroscopy.}\textsuperscript{23,45–48} All samples were placed into a nonluminescent cell mounted in a home-built liquid-nitrogen-cooled dewar whose bottom was made of quartz. The samples were cooled to 77 K to increase the signal intensity. Dried air was blown over the outside of the
quartz windows to avoid ice formation. The excitation pulse used was the fourth harmonic generation of a Nd/YAG laser (Quanta Ray, Spectra Physics) coupled with an optical parametric oscillator unit (Versa Scan and UV Scan) to convert the wavelength of the laser light to 394 nm. The fluorescence of the sample was collected at a right angle to the excitation beam and directed via two lenses into the entrance slit of the spectrometer (Shamrock RS 303i, 300 lines/mm, Andor Technology). The optically triggered signals from the PIN photodiode to the controller in the PC software were adjusted through a delay generator (DG535, Stanford Research Inc.). The resultant spectra were recorded with a time-gated ICCD camera (iStar, Andor Technology). The gate width was 25, 50, or 100 μs, and the delay time after the excitation laser pulse was 10 μs. Lifetime data were analyzed using the Origin (Light Stone) software. Details on the detection system can be found in recent refs.20,22

Interpretation of Eu3+ Luminescence Spectra and Theory.21,24,49,50 Although the theory was established by Judd and Ofelt independently in the early 1960s,51,52 the so-called J–O theory remains one of the most well-known theories among experimentalists for describing luminescence profiles (e.g., transition probability and energy level) of REEs. For the details of the mathematical derivation and the corresponding interpretation in the J–O theory, readers are referred to recent tutorials and brilliant reviews.21,24,49 Therefore, conclusive remarks based on these reviews are briefly summarized in the followings paragraphs.

In a recent review, Binemanns criticizes the use of ratio $R_{12}=I_{4}^{0}(7D_{0} \rightarrow 7F_{2})/I_{4}^{0}(7D_{0} \rightarrow 7F_{1})$ as an indicator useful for a probe in Eu3+-containing compounds because this could describe neither asymmetry nor structural distortion.21 Instead of using $R_{12}$, the shape analysis, which Kepert first introduced and Raymond and co-workers further developed for eight-coordinate RE complexes, gives more appropriate explanation.53,54 We agree on this; however, the book had yet to be written because the well-known coordination number for Eu3+ aquo ions is eight to nine, implying the limit of the model.

Our primary concern in the present work was to classify the sample ores, which are solid state, on the basis of their luminescence spectra. The use of Eu3+ ions as a structural probe is allowed in cases where Eu3+ ions are well isolated in the host matrix and no intermetallic interaction (i.e., Eu-to-Eu energy transfer or back transfer) occurs between neighboring Eu3+ centers.21 In this sense, the concentration of Eu3+ determined by ICP–OES (25 mg/kg) is sufficiently small for the Eu3+ ions to be well isolated from each other.

**AUTHOR INFORMATION**

**Corresponding Author**

Noboru Aoyagi — Advanced Science Research Center, Japan Atomic Energy Agency (JAEA), Ibaraki 319-1195, Japan; orcid.org/0000-0002-0913-2742; Email: aoyagi.noboru@jaea.go.jp

**Authors**

Thuy T. Nguyen — Institute for Technology of Radioactive and Rare Elements (ITRRE), VINATOM-MOST, Hanoi 94027, Vietnam

Yuta Kumagai — Nuclear Science and Engineering Center, JAEA, Ibaraki 319-1195, Japan; orcid.org/0000-0002-9149-0185

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