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Quantitative Phase Analysis of Preferentially Oriented Smectite Using the PONKCS / Rietveld Approach

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ABSTRACT

To achieve accurate quantitative phase analysis of scale containing amorphous silica and smectite, mixtures of silica gel and montmorillonite were quantified using the PONKCS/Rietveld method. The preferred orientation of montmorillonite was corrected using the March–Dollase function. As a result, the difference between the weighed and quantified values was approximately 2 mass%. The mixture samples, assuming the actual scale deposits, were successfully analyzed. The PONKCS/Rietveld method can accurately quantify not only crystalline phases but also amorphous silica and smectite with preferred orientation. This method enables a detailed understanding of the phase proportions in actual scale deposits and supports the selection of appropriate countermeasures based on quantitative analysis.

1 INTRODUCTION

Scale deposition causes serious operational problems in geothermal power plants and hot spring facilities. Scales are composed of various phases, including amorphous silica, smectite, sulfides, and carbonates (Ledésert et al., 2021; Manceau et al., 1995; Tut Haklidir and Haklidir, 2017; Wanyonyi et al., 2024). Each phase has distinct formation mechanisms and properties. Understanding their phase composition through qualitative and quantitative analysis is important for effective countermeasures. X-ray diffraction (XRD) is widely used for qualitative analysis, but quantitative phase analysis has been less investigated.

The Rietveld method (Rietveld, 1969), a powerful and widely used approach for quantitative phase analysis, relies on well-defined crystal structure models. It is difficult to apply this method to amorphous silica and smectite, which are commonly found in scale. Amorphous silica has a disordered structure, and smectite exhibits variations depending on its origin and hydration state, making it challenging to obtain accurate structural models for these phases. In addition, smectite is turbostratically disordered, having an asymmetric non-basal diffraction pattern. Its pattern is difficult to simulate by an ordinary Rietveld procedure (Wang et al., 2012; Wang et al., 2011). Consequently, the conventional Rietveld method is not sufficient for the quantitative analysis of scale containing amorphous silica and smectite.

To overcome these limitations, the PONKCS (Partial Or No Known Crystal Structures) method (Scarlett and Madsen, 2006) has been introduced (Itakura and Morita, 2025). This method creates a phase model that describes the diffraction patterns of amorphous silica and smectite, allowing them to be refined by the Rietveld method. This combined the PONKCS/Rietveld method successfully quantified both synthetic and actual scale samples. However, the previous study did not consider the preferred orientation of smectite, which may affect the accuracy of the quantitative results. The objective of this study is to improve the PONKCS/Rietveld method so that it can correct the preferred orientation of smectite in scale. To evaluate the accuracy of the improved method, mixture samples of amorphous silica and purified smectite, assuming actual scale samples, were analyzed.

2 EXPERIMENTAL

2.1 Instruments and samples

XRD data were collected using a MiniFlex II diffractometer (Rigaku Holdings Corporation, Japan) equipped with a D/teX Ultra2 detector. The instrument operated at 40 kV and 15 mA with Cu Kα radiation ($\lambda_{K\alpha1}$ = 1.5406 Å, $\lambda_{K\alpha2}$ =

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1.5444 Å). Measurements were conducted in flat-plate Bragg–Brentano θ–2θ geometry. The slit system consisted of a 0.625° divergence slit, an 8.00 mm scattering slit, and an open receiving slit. The scanning range, step size, and scan speed were 5–70° 2θ, 0.02°, and 0.3°/min, respectively. The total measurement time was approximately 4 hours. To prevent changes in (001) basal reflection caused by the interlayer water, the measurements were conducted at 473 K using BTS 500 Benchtop Heating Stage (Anton Paar Ltd., USA).

Mixture samples of amorphous silica and smectite were prepared using silica gel (Silica gel 60N, 40–50 μm, KANTO CHEMICAL CO., INC, Japan) and montmorillonite (Kunipia-F, KUNIMINE INDUSTRIES CO., LTD, Japan). The montmorillonite was a purified bentonite containing approximately 1–2 mass% quartz as an impurity, which was not distinguished in this study. The XRD patterns of each material are shown in Figure 1. Each sample was heated at 100 °C for 24 h to remove adsorbed and interlayer water. Samples were then weighed to a total of 0.5 g at the ratios shown in Table 1. All ratios presented in this paper are expressed in mass percentage. The mixture samples were homogenized by grinding and mixing in an agate mortar. In this paper, a sample containing n% montmorillonite is denoted as Mo-n (e.g., the mixture with 20% montmorillonite and 80% silica gel is referred to as Mo-20).

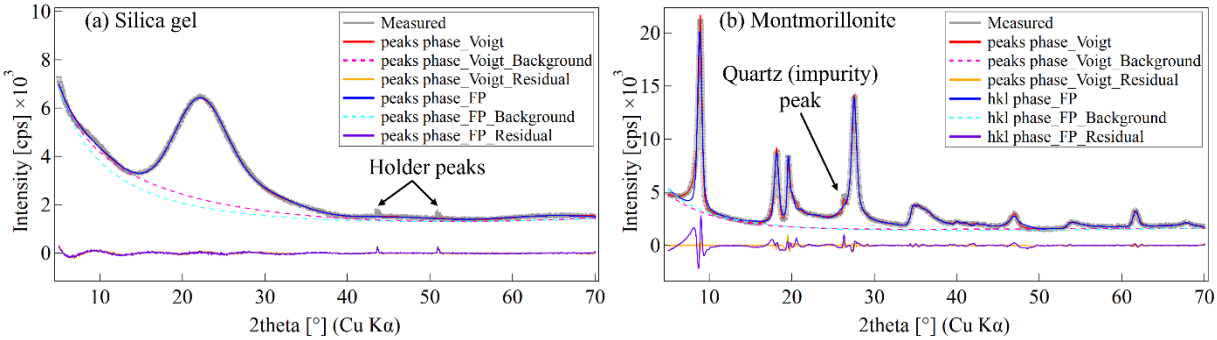


Figure 1. Measured and modeled diffraction patterns. (a) silica gel; (b) montmorillonite. Voigt: modeled using a split pseudo-Voigt function, FP: modeled using the Fundamental Parameters method.

Table 1. Compositions of the mixture samples.

Mass%	Mo-5	Mo-10	Mo-15	Mo-20	Mo-40	Mo-60	Mo-80	Mo-85	Mo-90	Mo-95
Silica gel	95	90	85	80	60	40	20	15	10	5
Montmorillonite	5	10	15	20	40	60	80	85	90	95

2.2 Quantitative phase analysis by the PONKCS/Rietveld method

2.2.1 PONKCS model

The Rietveld method is a whole pattern fitting approach, in which the diffraction pattern is theoretically calculated based on a well-defined crystal structure model. However, it is not easy to calculate a reliable theoretical pattern for our silica gel and montmorillonite because they have not been fully identified or structurally characterized. The PONKCS method provides a pseudo–model for such unknown phases, which can then be used in the Rietveld analysis. Two modeling approaches have been proposed (Scarlett and Madsen, 2006):

- peaks phase - This approach requires no structural information. The phase is represented by a series of peaks with arbitrary positions and intensities, which are refined to reproduce the measured diffraction pattern.
- hkl phase - This approach can be applied when the space group and lattice parameters are available. Peak positions are constrained by the space group and lattice parameters. Peak intensities are empirically refined against the measured pattern. Each reflection has an hkl index so that preferred orientation corrections can be done during Rietveld analysis.

In this study, the silica gel was modeled as a peaks phase, whereas montmorillonite was modeled as either a peaks phase or a hkl phase, and the results were compared. Both the peaks and hkl phase models were created by Pawley fitting (Pawley, 1981). The space group and lattice parameters for the hkl phase of montmorillonite

were taken from Gournis et al. (2008). The created models are shown in Figure 1. Quantitative analysis was performed for the mixture samples listed in Table 1 using two model combinations:

1. Silica gel (peaks phase) + montmorillonite (peaks phase), without preferred orientation correction.
2. Silica gel (peaks phase) + montmorillonite (hkl phase), with preferred orientation correction.

To evaluate the ability of the improved PONKCS/Rietveld method to correct the preferred orientation of smectite in the assumed scale samples, the quantitative results of cases 1 and 2 were compared.

2.2.2 Calibration of *ZMV* values

Quantification by the PONKCS/Rietveld method is based on the equation (1) proposed by Hill and Howard (1987):

$$W_i = \frac{S_i(ZMV)_i}{\sum_{j=1}^{n} S_j(ZMV)_j} \quad (1)$$

where *W*, *S*, *Z*, *M*, and *V* are the weight percentage, the Rietveld scale factor, the number of formula units per unit cell, the molecular mass of the formula unit, and the unit-cell volume, respectively. The scale factor *S* is refined during the Rietveld fitting, while the value of *ZMV* is theoretically calculated from the structural information.

Since the PONKCS models lack structural data, the *ZMV* value cannot be theoretically calculated and must be experimentally calibrated. The calibration is performed by Rietveld refinement of a mixture sample containing a standard phase with a *ZMV* value and an unknown phase without a *ZMV* value at a known weight ratio. For the mixture pattern, the diffraction pattern of the standard phase is calculated from its crystal structure data, while that of the unknown phase is calculated from the PONKCS model. Once the refinement yields the scale factors for both phases, the *ZMV* value of the unknown phase can be obtained as the only remaining variable in Equation (1).

In this study, the *ZMV* value of silica gel was calibrated using a 50:50 mixture of silica gel and corundum (Aluminum Oxide, Hayashi Pure Chemical Ind., Ltd, Japan), whereas that of montmorillonite was calibrated from a 40:60 mixture of montmorillonite and the previously calibrated silica gel (Mo-40).

2.2.3 Analysis procedure

The XRD data were analyzed using SmartLab Studio II (Rigaku Corporation, Japan). The split pseudo-Voigt function was used to create the peaks phases of silica gel and montmorillonite in case 1. The fundamental parameters method was used to create the peaks phase of silica gel and the hkl phase of montmorillonite in case 2. The background was calculated using a fourth-order LASSO optimization function, which is an improved version of the inverse power polynomial and is available in SmartLab Studio II. In the quantitative phase analysis, the refined parameters were the Rietveld scale factor, background, and peak shift. When the peak positions were not well fitted, the lattice parameters were also refined. In case 2, in addition to these parameters, the preferred orientation of the (001) basal reflection of montmorillonite was refined using the March–Dollase function. Due to the low bulk density of the silica gel, the X-ray absorption coefficient was weak. Sample holder peaks appeared at approximately 44° and 51° 2θ and these peaks were excluded from the quantitative analysis.

3 RESULTS

The mixture samples were quantified using case 1 (without preferred orientation correction) and 2 (with preferred orientation correction) by the PONKCS/Rietveld method. The quantitative phase analysis results are summarized in Table 2. For samples Mo-5 to Mo-40, the differences between the weighed and quantified values were within approximately 2% for both case 1 and 2. In contrast, for Mo-60 to Mo-95, the quantification error increased in case 1, where montmorillonite was overestimated by about 3–8%. In case 2, with preferred orientation correction, the errors were around 2% even for Mo-60 to Mo-95, although montmorillonite tended to be slightly underestimated. The fitting parameter R_{wp} indicates the degree of agreement between the measured and calculated diffraction patterns. In previous PONKCS/Rietveld studies (de Matos et al., 2022; Wang et al., 2012), R_{wp} values typically ranged from 3–9% and the values obtained in this study were comparable. Therefore, the fitting accuracy was sufficient in both cases. Notably, although R_{wp} generally decreases as quantification accuracy improves, in this study R_{wp} was lower in case 1 despite the higher quantitative accuracy achieved in case 2.

Table 2. Quantitative phase analysis results by PONKCS/Rietveld method. PO: preferred orientation, Mo: montmorillonite, Si-gel: silica gel.

Mass%	Weight value		Case 1, without PO correction			Case 2, with PO correction		
	Mont	Si-gel	Mont	Si-gel	R_{wp} [%]	Mont	Si-gel	R_{wp} [%]
Mo-5	5	95	3.88 (0.18)	96.12 (0.18)	3.34	5.78 (0.18)	94.22 (0.18)	2.91
Mo-10	10	90	9.36 (0.10)	90.64 (0.10)	3.21	11.30 (0.20)	88.70 (0.20)	3.32
Mo-15	15	85	15.78 (0.09)	84.22 (0.09)	3.07	15.86 (0.18)	84.14 (0.18)	3.09
Mo-20	20	80	19.24 (0.11)	80.76 (0.11)	3.43	20.70 (0.10)	79.30 (0.10)	3.78
Mo-40	40	60	40.14 (0.09)	59.86 (0.09)	2.59	38.68 (0.19)	61.32 (0.19)	3.89
Mo-60	60	40	63.01 (0.16)	36.99 (0.16)	3.70	58.10 (0.20)	41.90 (0.20)	5.52
Mo-80	80	20	88.40 (0.30)	11.60 (0.30)	6.04	80.00 (0.40)	20.00 (0.40)	7.65
Mo-85	85	15	91.10 (0.30)	8.90 (0.30)	5.10	84.10 (0.40)	15.90 (0.40)	7.42
Mo-90	90	10	95.20 (0.30)	4.80 (0.30)	5.00	88.10 (0.40)	11.90 (0.40)	7.71
Mo-95	95	5	97.14 (0.18)	2.86 (0.18)	2.93	93.30 (0.40)	6.70(0.40)	7.60

The fitting results were shown in Figures 2 and 3 for cases 1 and 2, respectively. In case 1, the (001) basal reflections (Figure 2(a, b)) were well reproduced by the model. The diffraction patterns between 10° and 70° 2θ (Figure 2(c, d)) were also fitted well, but larger residuals were found around 20° and 35° 2θ for samples Mo-40 to Mo-95. These residuals indicated an overestimation of the peak intensities.

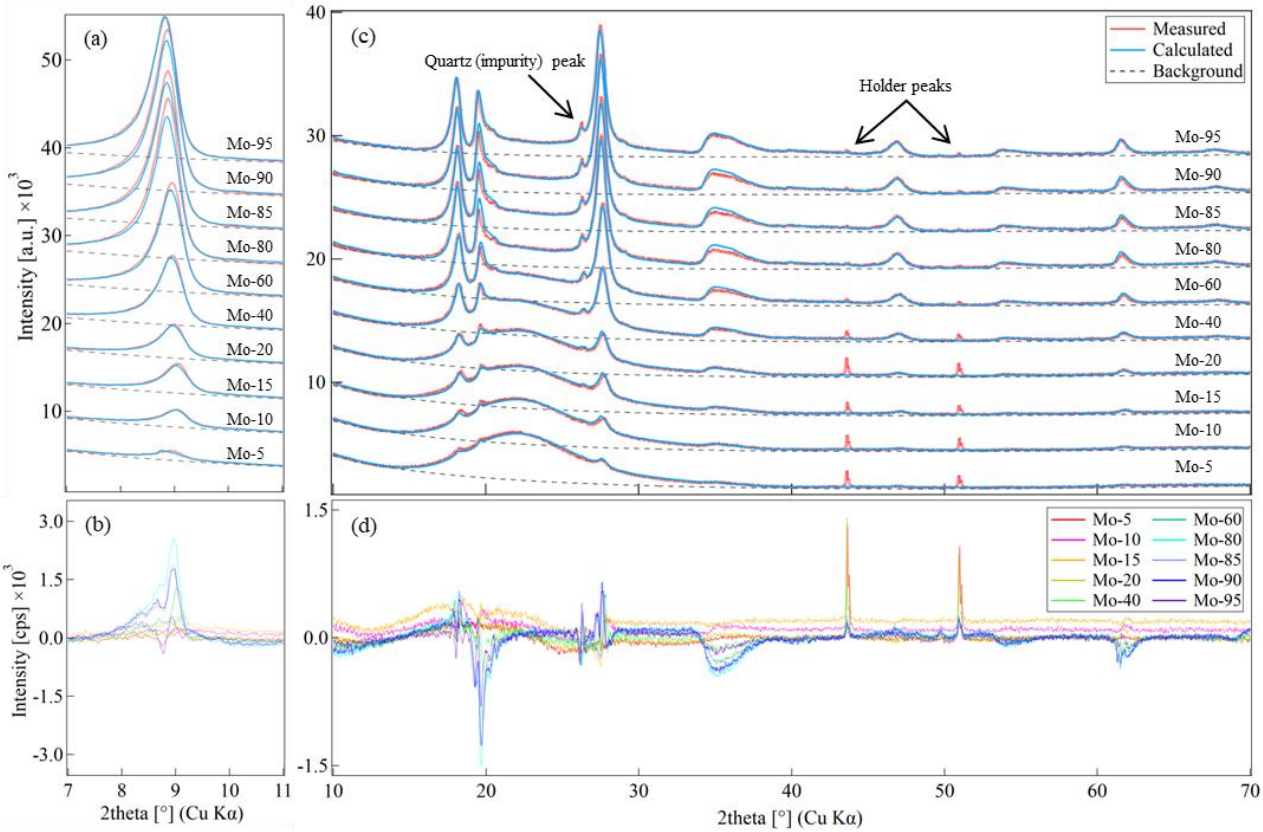


Figure 2. Fitting results obtained by the PONKCS/Rietveld method. Case 1: silica gel (peaks phase) and montmorillonite (peaks phase), without preferred orientation correction. (a) 001 basal peak, (b) residual of 001 basal peak fitting, (c) fitting in the 10–70° 2θ range, (d) residual of fitting in the 10–70° 2θ range.

In case 2, with preferred orientation correction, the (001) basal reflections (Figure 3(a, b)) showed a larger misfit in peak position compared with case 1, and the peak tail was not well reproduced. In contrast, the fitting between 10° and 70° 2θ (Figure 3(c, d)) showed good agreement. The residuals around 20° and 35° 2θ were smaller than case 1.

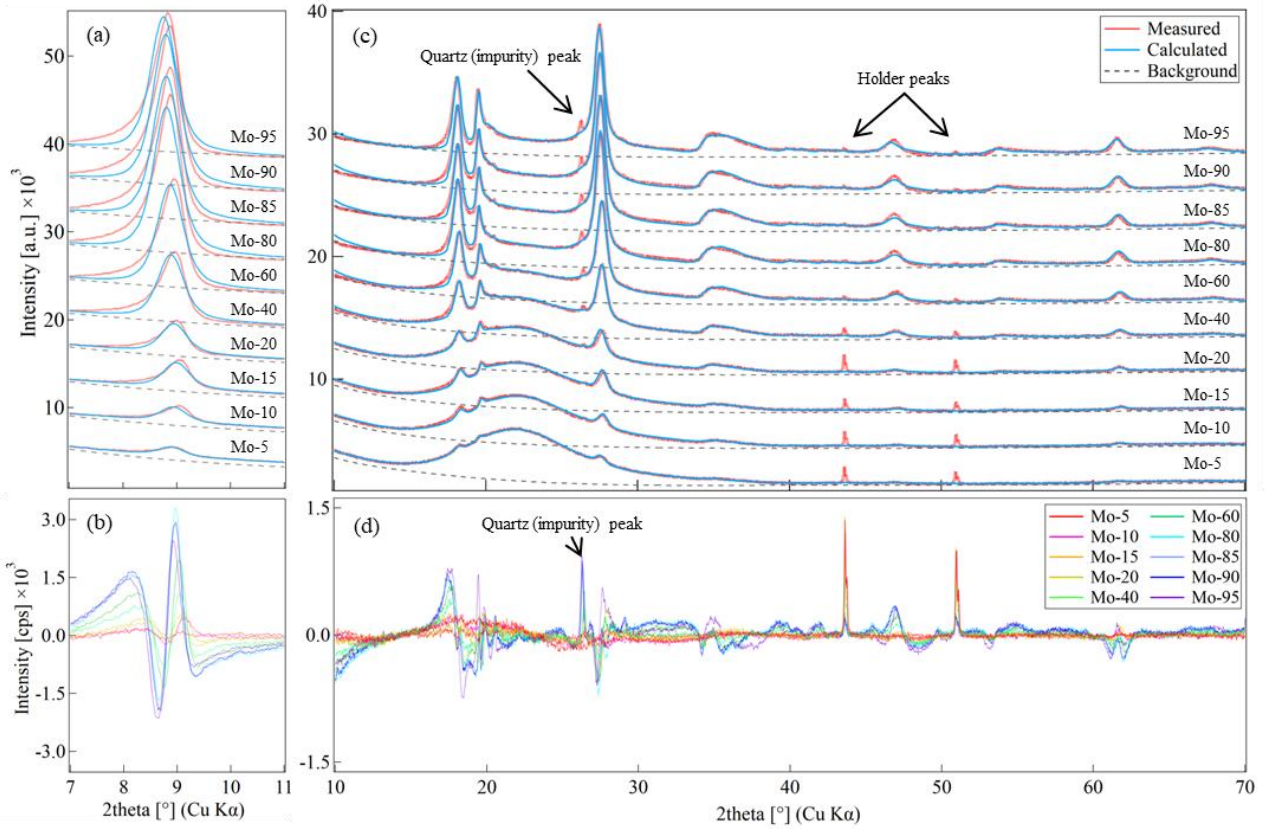


Figure 3. Fitting results obtained by the PONKCS/Rietveld method. Case 2: silica gel (peaks phase) and montmorillonite (hkl phase), with preferred orientation correction. (a) 001 basal peak, (b) residual of 001 basal peak fitting, (c) fitting in the 10–70° 2θ range, (d) residual of fitting in the 10–70° 2θ range.

4 DISCCUSION

In case 1, when preferred orientation correction was not applied, montmorillonite was overestimated in the Mo-60 to Mo-95. Although the (001) basal peaks were fitted well, the calculated montmorillonite peak intensities were higher than the measured ones around 20° and 35° 2θ in the 10–70° 2θ range (Figure 2). This suggests that the strong (001) reflection, enhanced by preferred orientation, affected the overall calculated pattern. Consequently, the scale factor was overestimated, leading to an overestimation of montmorillonite content. In contrast, for Mo-5 to Mo-40, the quantitative errors were small because the smaller amount of montmorillonite reduced the relative influence of preferred orientation.

In case 2, when preferred orientation correction was applied, all samples were quantified within approximately 2% error. The (001) basal peaks of case 2 showed larger residuals compared with case 1 (Figure 3(a, b)). As shown in Figure 1(b), the calculated pattern of the montmorillonite hkl phase deviated more from the measured pattern than that of the peaks phase. This mismatch in the PONKCS model likely affected the fitting of the mixture samples. The deviation in the hkl phase model may be caused by differences between the assumed space group or lattice parameters and those of the actual sample. The montmorillonite used in this study differs from that reported by Gournis et al. (2008) in locality and chemical composition. By optimizing the space group and lattice parameters, the accuracy of the PONKCS model could be improved. Although a mismatch was observed in the (001) reflection, it had little effect on the quantitative results. However, when a scale contains several clay minerals, such model errors may have a larger impact and should be carefully considered. In the 10–70° 2θ range (Figure 3(c, d)), the measured and calculated patterns in case 2 matched well, and no significant regions with overestimated peak intensities were found. This result suggests that the preferred orientation of the (001) plane was properly corrected by the March–Dollase function, improving the overall fitting quality. The large R_{wp} values may be attributable to the deviation of the 001 basal peak. Nevertheless, the R_{wp} values were

sufficiently small, and the correction of preferred orientation was considered more significant than the 2–4% difference in R_{wp} between case 1 and 2.

The previous studies applied the PONKCS/Rietveld method to quantify amorphous supplementary cementitious materials (SCMs) in Portland cement and reported an accuracy of approximately 1–3% (de Matos et al., 2022; Snellings et al., 2014). In this study, a similar accuracy was achieved by applying preferred orientation correction. The montmorillonite used in this study was relatively well-crystallized and therefore more affected by preferred orientation. In contrast, smectite that precipitates as geothermal scale deposits are usually poorly crystalline (Aramaki et al., 2005; Kasai et al., 2000; Manceau et al., 1995), and the orientation effect is expected to be smaller. Thus, the findings of this study are expected to enable more accurate quantification of smectite in actual scale deposits.

5 CONCLUSION

In this study, to achieve accurate quantitative phase analysis of scale containing amorphous silica and smectite, mixtures of silica gel and montmorillonite were quantified using the PONKCS/Rietveld method. The preferred orientation of montmorillonite was corrected using the March–Dollase function. The results were as follows:

- The preferred orientation was successfully corrected using the March–Dollase function, and the difference between the weighted and quantified values was approximately 2%.
- Without preferred orientation correction, in the samples containing 60–95% montmorillonite (Mo-60 to Mo-95), the montmorillonite content was overestimated by 3–8%.

The PONKCS/Rietveld method could correct the preferred orientation of montmorillonite and provide accurate quantitative results. This method is expected to enable quantitative analysis of actual scale deposits containing not only crystalline phases but also amorphous silica and smectite with preferred orientation.

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