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Magnetic Characteristics of Ancient Plain Coarse Pottery and Pantiles from Cheju Island

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Cheju island is composed of volcanic tuff. The soil in Cheju island has principally sprung from basalt and partially made up of trachyte, and andesite. Also ancient relics, plain coarse pottery kilns and pantiles kilns are homogeneously distributed all over the Cheju island. In this study samples of plain coarse pottery and pantiles from five regions of Cheju island have been examined through X-ray fluorescence spectrometer and Mössbauer spectroscopy. It is thought that these samples be partially formed from neutral volcanic rock like trachyte and the valence state of iron is almost Fe^{3+}. Also the magnetic hyperfine field of goethite contained in these samples is less than synthetic goethite. This result shows the degradation of magnetic order caused by the partial substitution of diamagnetic positive ion Fe^{3+} by Al^{3+} in the goethite lattice.

1. Introduction

Cheju island is composed of volcanic tuff, produced by frequent volcanic activity during the periods from the Cenozoic 3rd era to the 4th era. The soil on Cheju island has principally sprung from basalt and partially from trachyte and andesite. Also it is thought that the present Cheju island formed from repeated eruptions throughout the island, which was originally coupled with the continent, made a large mountain and later changed into an island [1].

Remains and relics on Cheju island are found in all parts of island through each era, such as the Aeuumli cave site in the paleolithic period to the Kosanri pre-historic site in the neolithic period and Sangmori site of undetermined age. Also many plain coarse pottery kilns and pantiles kilns are distributed all over Cheju island [2]. Plain coarse pottery and pantiles are vessels made of clay by firing and are well-preserved archaeological relics despite their long sedimentation environment. They are basic archaeological specimens, from which it is possible to estimate the production process or technique and environment. It is required in these days to develope science and technology in order to obtain information about variable cultures and technical levels in that period through examination of pottery and pantiles.

Studies of plain coarse pottery and ceramics may deal with their raw material, the production centers the temperature and atmosphere of firing [3-8], While little work of this kind has been done in samples of Cheju island.

Therefore, the object of this study is to analyze the minerals contained in plain coarse pottery excavated in the Aewolup Hangmong historical site, Cheju city's Chejumok Kwanaji historical site, and pantiles excavated in the Kosanri pre-historic site, the Bookchonri site, and the Samyangdong site, using an X-ray fluorescence spectrometer, and to find their magnetic properties using Mössbauer spectroscopy.

2. Inspection

2.1 Locations of sample

Plain coarse pottery used this study are discovered in the Kosanri pre-historic site (P1), excavated in the Bookchonri site (P2), and in the Samyangdong site (P3), pantiles used this study is excavated in the Aewolup Hangmong historical site (T1, T2), and in the Cheju city Chejumok Kwanaji his-

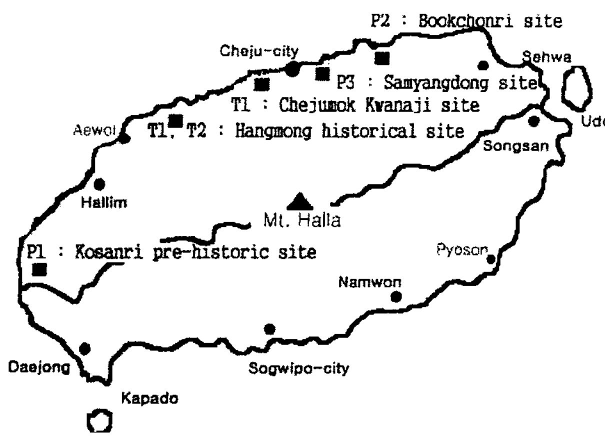

Fig. 1. Plain coarse pottery and pantiles sample locationsin Cheju island.

torical site (T3) Fig. 1. shows the area in which plain coarse pottery and pantiles are discovered.

2.2 Sample preparation

Samples of plain coarse pottery and pantiles used in this study were washed and dried, and then made into powder (about 100 mesh) for the X-ray fluorescence and Mössbauer spectroscopy.

3. Experimental Preparation

3.1 X-ray fluorescence spectrometer

X-ray fluorescence spectrometry was carried out at the Inter-University Centers of Natural Science Research Facilities in the Seoul National University. The analytical instruments was a Shimadzu XRF-1700 Sequential X-ray fluorescence spectrometer, with the x-ray tabe operated at 40 kV and 30 mA, using a solvent ($Li_2B_5O_7$, lithium tetraborate) weighing 7 gms. And it is weighted by a drawing on a calibration curve.

3.2 Mössbauer spectroscopy

The Mössbauer spectroscose used in this experiment (S-600 made by Austin Co., USA) is of the equivalent-accelated type. Measured data can be stored on a PC hard disk. A refrigerated device, made by APD company, is combined CS-202 Displex with a DMX-20 Mössbauer vacuum shroud. A compressure circulates He gas, and the sample is cooled by a gas transmission heat exchanger in the shroud.

The Mössbauer spectrum is measured, using electrodynamic equivalent-accelated type Mössbauer spectrometer. The γ-ray source is a 10 mCi of ^{57}Co by DuPont Co., electro deposited in rhodium at room temperature. For measuring the Mössbauer spectrum, first the sample powder is compressed in a sample holder and evacuated to a pressure of the 10^{-5} Torr.

While Mössbauer spectrum is recorded out, the distance between the sample and the detector is kept at 120 mm. The Doppler velocity is ± 16 mm/s. The a Mössbauer spectrum is fitted by a least square technique using a Lorentzian function.

4. Result and Analysis

4.1 X-ray fluorescence Analysis

The chemical composition of plain coarse pottery and pantiles gathered in five regions on Cheju island determined by X-ray fluorescence analysis is shown in Table 1.

The content of SiO_2 of plain coarse pottery and pantiles is from 51.59 wt% to 71.96 wt%, which is higher than the content of SiO_2 in clay of volcanic ash which has principally formed from basic basalt. The content of Al_2O_3 is analysed from 15.71 wt% to 20.85 wt%, which is lower than the Al_2O_3 content of clay of volcanic ash – 26.70 wt% to 34.09 wt%. The contents of Fe_2O_3 also lower, – 4.03 wt% to 11.49 wt%. Also, through Table 1, it can be seen that ion of Si and Al are much greater at all plain coarse and pantiles sample of the five regions, while the content of magnetic ion, Ti and Mn is very low.

Especially, the content of Fe_2O_3 in plain coarse pottery and pantiles in the five regions used in this study is doesn't lower than the content of Fe_2O_3 found in clay of volcanic ash on Cheju island reported by Shin and Tavernier [9] and Song and Yoo [10]. Also, the content of SiO_2 was high and the content of Fe_2O_3 was analysed as low. From this result, it is thought that the soil used in making plain coarse pottery and pantiles excavated in the five regions used in the study comes from basalt containing much iron inclusion from old soil minerals, but formed partially as used in the study from neutral volcanic rock like trachyte. This estimate is the same as the result of the study about the soil on Cheju island by Kang [11].

4.2 Mössbauer spectrum analysis

To analyze the doublets and sextets appearing in the Mössbauer spectra we used the linear equation of the Lolentzian

$$y=\frac{1}{2\pi}\sum_{i=1}^{N=6}\frac{A_i\Gamma_i}{(x-V_i)^2+\left(\frac{\Gamma_i}{2}\right)^2} \quad (1)$$

and fitted each spectrum by computer using a least square

Table 1. Chemical composition of plain coarse pottery and pantiles by XRF

Component / Sample NO	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	MnO	P_2O_5	L.O.I	Total
P1 (Kosan)	51.59	20.85	11.49	2.21	1.03	2.09	2.07	2.18	0.06	1.11	5.39	100.07
P2 (Bookchon)	56.59	19.52	8.63	2.78	1.41	2.05	1.55	1.56	0.06	0.27	5.61	100.03
P3 (Samyang)	55.91	19.72	8.02	1.48	1.07	2.00	1.57	2.11	0.08	2.65	1.17	101.02
T1 (Hangmong)	64.67	16.18	7.23	0.74	1.51	2.11	1.51	1.26	0.08	0.18	4.41	99.87
T2 (Hangmong)	68.25	15.42	8.67	0.55	1.76	2.00	1.27	1.91	0.13	0.15	0.52	100.62
T3 (Mokkwanaji)	68.67	15.84	7.39	0.64	1.70	2.12	1.24	1.30	0.07	0.23	0.64	99.84

LOI (Loss Of Ignition) : the difference in wt% between before-burning and after -burning at 950 °C

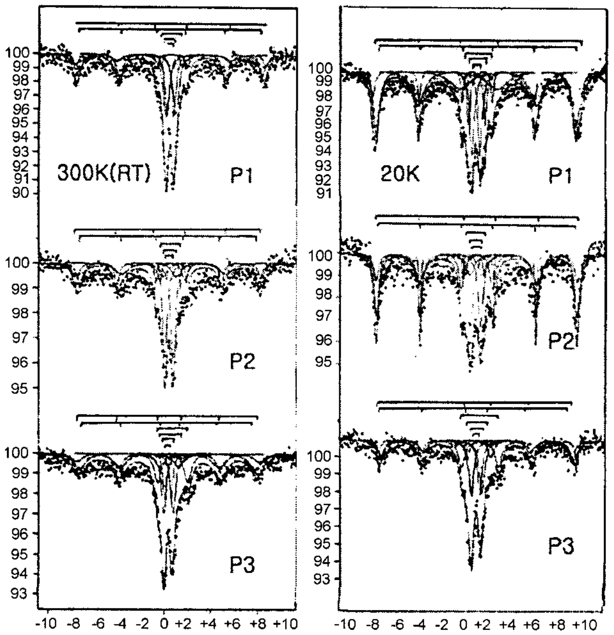

Fig. 2. The Mössbauer spectra of plain coarse pottery at 300 K and 20 K.

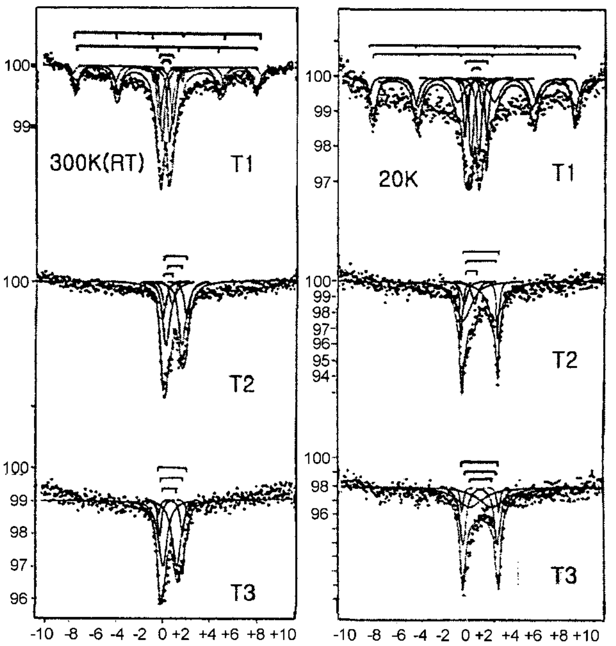

Fig. 3. The Mössbauer spectra of pantiles at 300 K and 20 K.

fitting technique. In Eq. (1) A_i, Γ_i, V_i, are area, thickness of line, position of resonance absorption line i, and N is the number of resonance absorption lines. We can get the isomer shift, the shift of the electric quadrupole, and the hyperfive magnetic field from this equation. We took Mössbauer spectra at 300 K and 20 K as shown in Figs. 2 and 3, and the Mössbauer parameters obtained from the Mössbauer spectra are shown in Table 2.

1) Isomer Shift

From Mössbauer spectra obtained at 300 K and 20 K the isomer shift of doublets ranges from 0.175 mm/s to 0.623 mm/s, with no consistent variation for samples from different locations. In the case of pantiles, T1 ranges from 0.263 mm/s to 0.332 mm/s and T2, T3 from 0.829 mm/s to 0.997 mm/s. All these values are within the range consistent with Fe^{3+}.

The isomer shift of doublets is higher at 20 K than at 300 K.

We conclude that the ionization state of ion in the plain coarse pottery and pantiles samples is entirely almost Fe^{3+}, but Fe^{2+} doublets are hardly observed.

2) Quadrupole splitting

The quadrupole splitting ranges from 0.472 mm/s to 2.589 mm/s, with correlation to the source of the samples. In the case of pantiles, the values range from 0.250 mm/s to 1.775 mm/s. In T2, T3 the values range from 0.647 mm/s to 2.426 mm/s, so the degrees in T2, T3 are larger than that in T1 as for the I. S. shifts, but this quadrupole splitting values show symmetry of the magnetic field slope of ^{57}Fe, which depends on electrons and ions existing near the nucleces. From this result, the mineral composition in ferrihydrite is very similar to superparamagnetism goethite and silicate clay minerals in a sample ore of excavated plain coarse pottery and pantiles.

3) Magnetic hyperfine field

The magnetic hyperfine field strength from the Mössbauer spectra can be calculated from 475.282 kOe to 496.486 kOe. The magnetic hyperfine field strength for hematites is calculated from 475.282 kOe to 496.486 kOe. In the case of pantiles, magnetic hyperfine field length of goethite in T1 is calculated 473.949. In T2, T3, the length cannot be calculated, so it seems special. In case of I. S. and Q. S. length, therefore, more consistent, various study on the producted time of pantiles, their sorts, etc. is required.

Magnetic hyperfine field strength of goethite contained in the pantiles samples at 300 K is less than 505 kOe obtained of pure goethite. The phenomenon has been reported also by Graham [12] *et al.*, Vanderberghe *et al.* [13] and Wang *et al.* [14] who indicated that magnetic hyperfine field strength in goethite and hematites in soil samples is normally less than synthetic goethite. The reason for this is partial substitution of Fe^{3+} (ion diameter 0.51 Å) by Al^{3+} (ion diameter 0.51 Å) in the goethite lattice, effecting the magnetic hyperfine splitting. This fact is proved by the result of a Mössbauer experiment, that as the amount of diamagnetic Al^{3+} in synthetic goethite and hematites is increased, the magnetic hyperfine field strength is linearly decreased [15].

Structural iron (Fe^{3+} and Fe^{2+}) in normal soils does not exist as independent oxide, but as material substituted for positive ion like Al^{3+}, Si^{4+} which have a similar coordination number in the crystal structure of clay mineral. So when plain coarse pottery and pantiles from clay are fired under changes in crystal structure, and their Fe ions also undergo changes in bonding.

Table 2. Mössbauer parameters of Cheju plain coarse pottery and pantiles in 5 regions at 300 K and 20 K

Sample NO	Temper-asure (K)	Fe^{3+} doublet		Fe^{3+} doublet		Fe^{3+} doublet		Fe^{3+} doublet		Goethite			Hepatite		
		I.S.	Q.S.	I.S.	Q.S.	I.S..	Q.S.	I.S.	Q.S.	I.S.	Q.S.	H_{hf}	I.S.	Q.S.	H_{hf}
		mm/s	mm/s	mm/s	mm/s	mm/s	mm/s	mm/s	mm/s	mm/s	mm/s	KOe	mm/s	mm/s	KOe
P 1	300	0.320	1.753	0.301	0.804	0.259	0.564			0.273	-0.203	496.486	0.343	-0.166	510.525
	20	0.420	2.511	0.388	1.397	0.336	0.671			0.339	-0.121	517.616	0.393	-0.131	540.128
P 2	300	0.382	1.771	0.218	0.917	0.175	0.472			0.336	-0.278	480.157	0.252	-0.121	498.157
	20	0.390	1.268	0.277	0.988	0.273	0.740			0.413	-0.181	529.670	0.383	-0.122	529.670
P 3	300	0.549	2.589	0.623	2.635	0.264	0.801	0.221	0.546	0.244	-0.176	475.282	0.283	-0.162	492.513
	20	0.572	3.097	0.692	3.144	0.385	0.958	0.334	0.689	0.417	-0.153	504.000	0.399	-0.023	521.231
T 1	300	0.332	1.775	0.263	0.523	0.250				0.284	-0.206	473.949	0.356	-0.168	493.949
	20	0.445	1.780	0.364	1.202	0.394				0.319	-0.183	508.164	0.371	-0.194	528.554
T 2	300	0.868	2.025	0.829	1.345	0.272	0.647								
	20	0.873	2.959	0.850	2.543	0.301	0.832								
T 3	300	0.997	2.426	0.836	1.928	0.716	1.177								
	20	0.898	3.000	0.900	2.811	0.942	1.803								

5. Conclusion

Through X-ray fluorescence analysis and Mössbauer spectoscopy at 300 K and 20 K, plain coarse pottery from five regions used in this study have very low FeO_3 content as compared with that known for clay from volcanic ash of Cheju island and have higher SiO_2 content and lower Al_2O_3 content. From this result, it is thought that samples of plain coarse pottery and pantiles in those five regions are not made from basalt, containing high iron old soil mineral content, but from partially neutral volcanic rock like trachyte. The iron ions are found to be Fe^{3+} . The fact that the magnetic hyperfine field of goethite contained in the pantiles samples excavated is less than in a synthetic goethite shows partial substitution of diamagnetic positive ion containing Fe^{3+} (ion diameter 0.51 Å) by Al^{3+} (ion diameter 0.51 Å) in the goethite lattice.

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