T-2

A research of Cheju Island plain coarse pottery and pantiles magnetism characteristic

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Abstract

Cheju Island has a nature of typical trass through volcanic activities in many times. The soil in Cheju Island has principally sprung from basalt and partially made up of trachyte, trachyte's nature and site. Also ancient relics, plain coarse pottery's kilns and pantiles kilns are homogeneously distributed all over the Cheju Island.

In this study, as a result of X-ray fluorescence spectrometer and Mössbauer spectroscopy of a sample are from plain coarse pottery and pantiles in 5 regions of Cheju Island. It is thought that these samples are partially formed from neutral volcanic rock like trachyte and Atomicity State of iron is almost Fe^{3+}. Also the magnetic hyperfine field length of goethite, contained these samples is less than synthetic goethite magnetic hyperfine field length and this result shows that disintegration of inner magnetic order, created by partial substitution of diamagnetic positive ion containing Fe^{3+} and Al^{3+} in goethite lattice.

Ⅰ. Introduction

Cheju Island has a nature of typical trass through volcanic activities in many times during periods from the Cenozoic 3rd era to the 4th era and the soil in Cheju Island has principally sprung from basalt and partially from trachyte, trachyte's nature and site. Also it is estimated that present Cheju Island formed from repeated condition through the Island had coupled with a continent, changed in large range then changed into an Island.

For remains and relics based on cultural heritage in Cheju Island, they are discovered in each part of the Island through each era like Aeuumri cave site in the paleolithic period to Kosanri pre-historic site in the Neolithic period and Sangmori site in the have not a figure age. Also many plain coarse pottery's kilns and pantiles kilns are distributed all over Cheju Island and as for plain coarse pottery or pantiles they are vessels made of clay by baking and well-preserved archaeological relics despite of long sedimentation environment. Because they are basic archaeological specimen that can make it possible to estimate production process or technique and environment, it is required in these days to develop science and technique in order to obtain information about variable culture and technique level through crackers or pantiles.

Under this situation, studies about plain coarse pottery and ceramics of internal and external nation dealing with their raw material, the production center, the beginning, the temperature and atmosphere while baking, make lively process but studies about plain coarse pottery in Cheju Island or information about their physical and chemical characteristic and about tile are little known.

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

Ⅱ. Inspection

1. Sample findspot

Plain coarse plain coarse pottery used this study are discovered in Kosanri pre-historic site(P1), excavated in Bookchonri site(P2), and in Samyangdong site(P3), pantiles used this study is excavated in Aewolup Hangmong historical site(T1, T2), in Cheju city Chejumok Kwanaji historical site(T3) Fig 1. shows the area in which Plain coarse plain coarse pottery and pantiles are discovered.

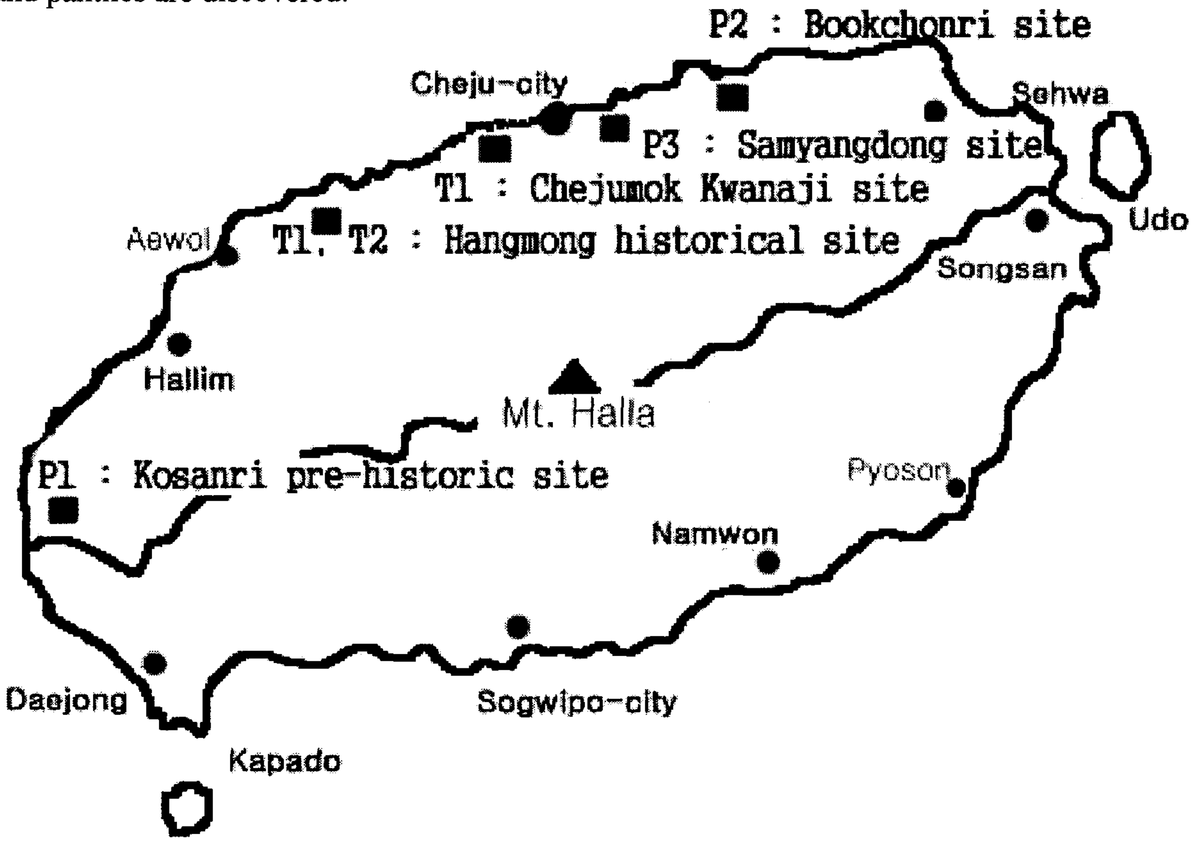

Fig 1 : Cheju Island plain coarse pottery and pantiles sample findspot

2. Making a sample ore

To investigate ingredient of plain coarse pottery and pantiles used in this study, they are washed and dried out. Next they are made into powder(about 100 mesh) to use for sample ore for X-ray fluorescence spectrometer and Mössbauer spectrum measuring.

3. The method of experiment

1) X-ray fluorescence spectrometer

X-ray fluorescence spectrometer is requested for Inter-University Centers of Natural Science Research Facilities in Seoul National University. The analytical instruments are Shimadzu XRF-1700 Sequential X-ray fluorescence spectrometer. Voltage is conditioned to 40 kV and an electric current is 30 mA, Diagnosis is carried out by X-ray injection using Rh target. Glass bead sample is made by compounding a sample ore ignition in 950 ℃ and a solvent($Li_2B_5O_7$, lithium tetraborate) 7 g and it is weighted by drawing up a calibration curve.

2) Mössbauer spectroscopy

Mössbauer spectroscopy used in this experiment(s-600 made by Austin co. in America) is equivalent-accelerated type and controlled by control system. Measured data can be stored in PC harddisk. A refrigerated device, which is produced by APD co. , is combined CS-202 displex and DMX-20 Mössbauer vacuum shroud . A compressor that circulates He gas operates it . The sample ore part is colded by gas transmission heat exchanger reciprocation in shroud

Mössbauer spectrum is measured, using electro dynamic equivalent-accelerated type Mössbauer spectrometer. γ-ray material is measured using 10 m Ci ^{57}Co unary ray material , produced by Du font co. , electro deposited in rhodium at room temperature. To measuring M?sbauer spectrum , first a sample ore is compressed and fixed using sample holder made of copper, in a thermostats. Next by vacuum device, it is ventilated till 10^{-5} Torr, and measured.

While Mössbauer spectrum measuring is carried out, the distance between a sample ore and a detector is kept to 120 ㎜ , Doppler velocity is kept to ± 16 ㎜/s

Also Mössbauer spectrum is measured by least square fitting technique using Lorentzian function.

Ⅲ. Result and Analysis

1. X-ray fluorescence Analysis

Chemical composition of plain coarse pottery and pantiles particles gathered in 5 region in Cheju Island that is analyzed by using X-ray fluorescence Analyzer shows in Table 1.

Through Table 1, content of SiO_2 of plain coarse pottery and pantiles particle is from 51.59 wt% (at least) to 71.96 wt%(at most), so if shows higher than content of SiO_2 in clay of volcanic ash which has principally formed from basic basalt and content of Al_2O_3 is analyzed from 15.71 wt% to 20.85 wt% , which shows lower degree than content of Al_2O_3 of clay of volcanic ash, 26.70 wt% to 34.09 wt% , and content of Fe_2O_3 also shows low degree, 4.03 wt% to 11.49 wt%. Also through Table 1, It can be seen that ion of Si and Al are contained much at all plain coarse and pantiles sample of 5 region while content of magnetic ion, Ti and Mn is very low.

Especially, content of Fe_2O_3 in plain coarse pottery and pantiles in 5 region used at this study was lower than content of Fe_2O_3 shown at the study about clay of volcanic ash in Cheju Island attained by Shin, Tavemier(1988) and Song[10], Yoo(1991)[11]. Also content of SiO_2 was high and content of Fe_2O_3 was analyzed low. From this result, it is thought that soil used in making plain coarse pottery and pantiles excavated in 5 regions used in the study from basalt, containing much iron inclusion old soil minerals, but formed partially the used in study from neutral volcanic rock like trachyte. This estimate is same for the result of study about soil in Cheju Island by Kang (1997) [9]

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

※LOI(Loss Of ignition) : the difference in wt% between before-burning and after -burning at 950 ℃

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	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	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	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	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	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	68.67	15.84	7.39	0.64	1.70	2.12	1.24	1.30	0.07	0.23	0.64	99.84

2. Mössbauer spectrum analysis

To make detailed analysis of doublets and sextets appearing from Mössbauer effect about plain coarse pottery and pantiles excavated in specific 5 remains in Cheju Island, we used linear equation of Lolentzian

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

and fitted each spectrum by computer using least square fitting technique. And in the equation(1) A_i, Γ_i, V_i, each means area, thickness of line, position of resonance absorption line at i times and N means the number of resonance absorption line. Because we can get movement of isomer, the movement distance of electric quadruple and hyper-minute magnetic field from this equation, we took Mössbauer spectrum at 300 K and 20 K about plain coarse pottery and pantiles sample excavated in specific 5 remains in Cheju Island, which is shown in Fig 2, Fig 3, and degrees of Mössbauer parameter obtained from Mössbauer spectrum are shown in Table2.

1) Isomer Shift

From Mössbauer spectrum obtained by 300 K and 20 K about plain coarse pottery sherd and pantiles shown in Fig 2 and Fig 3, the degree of isomer shift of doublets shows the scope of 0.175 mm/s to 0.623 mm/s , so it is thought that the special change caused by different region does not seem to exist. Meanwhile , in the case of pantiles , T1 shows its scope of 0.263 mm/s to 0.332 mm/s and T2, T3 does of 0.829 mm/s to 0.997 mm/s that in the case of T2 and T3, the degree of isomer shift shows higher value than that of T1. But it can be known that the degree of Isomer shift is still in the scope of the degree of Fe^{3+}.

Also, from Mössbauer spectrum obtained at 20 K we can know that the degree of isomer shift of doublets shows higher than the degree of that at 300 K like Table 2.

From this, it can be known that the state of ion existing in plain coarse pottery and pantiles sample in the 5 region in Cheju Island is almost Fe^{3+} and Fe^{2+} doublets is hardly observed.

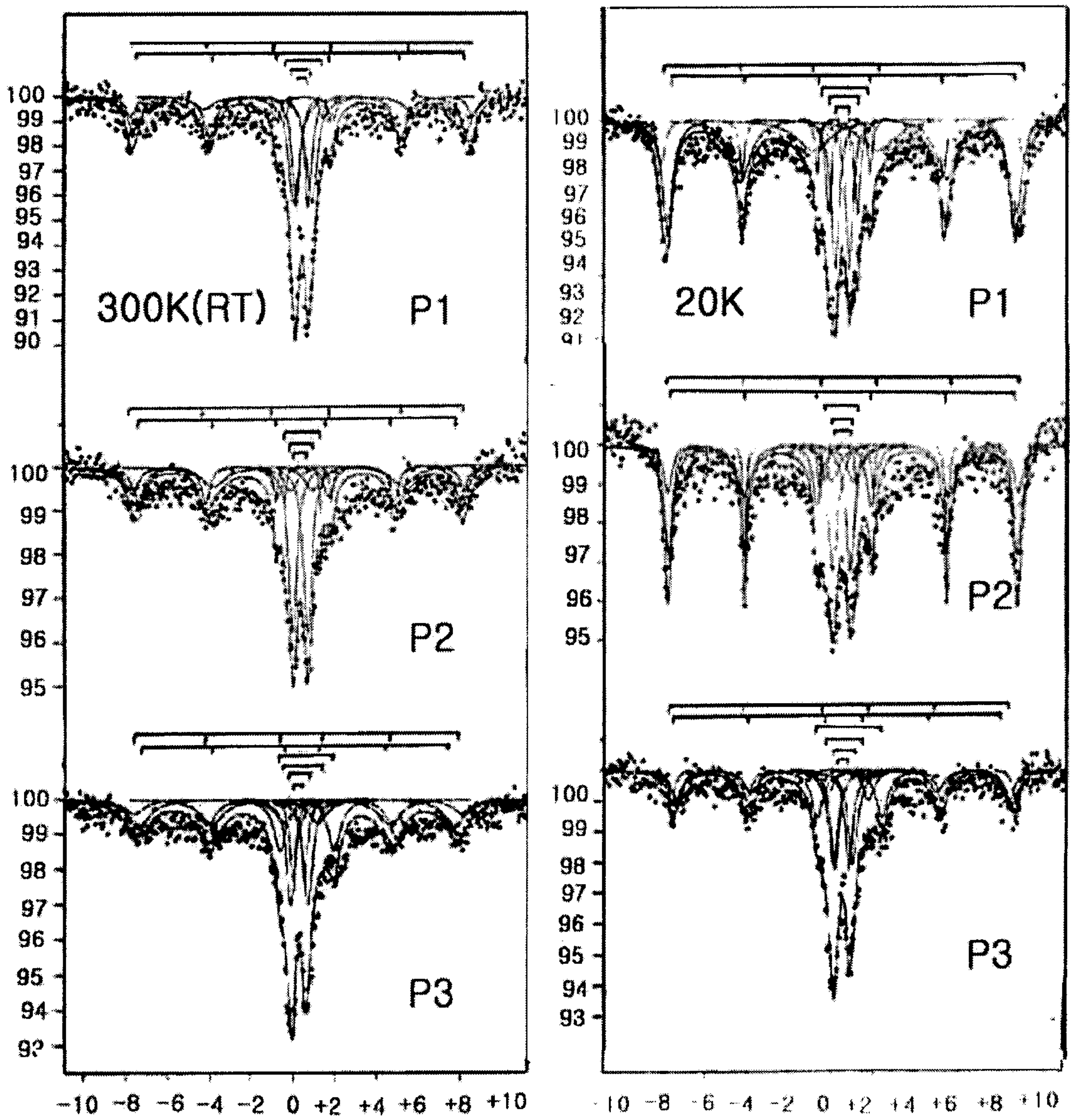

Fig 2 . The spectra of plain coarse pottery at 300 K and 20 K

2) Quadrupole splitting

Quadrupole splitting degree obtained Mössbauer spectrum from plain coarse pottery sherd and pantiles excavated in 5 regions have a scope from 0.472 ㎜/s to 2.589 ㎜/s So it is concluded that there is little difference according to the place excavated. A case of pantiles the degrees range from 0.250 ㎜/s to 1.775 ㎜/s In T2, T3 the degrees range from 0.647 ㎜/s to 2.426 ㎜/s the degree in T2 , T3 are larger than that in T1 like I. S. but because this Quadrupole splitting degree show symmetry of magnetic field slope of 57Fe, it depends on electrons and ions existing near nuclear. From this result, mineral composition in ferrihydrite is very similar to superparamagnetism goethite and silicate clay mineral in a sample ore of excavated plain coarse pottery and pantiles.

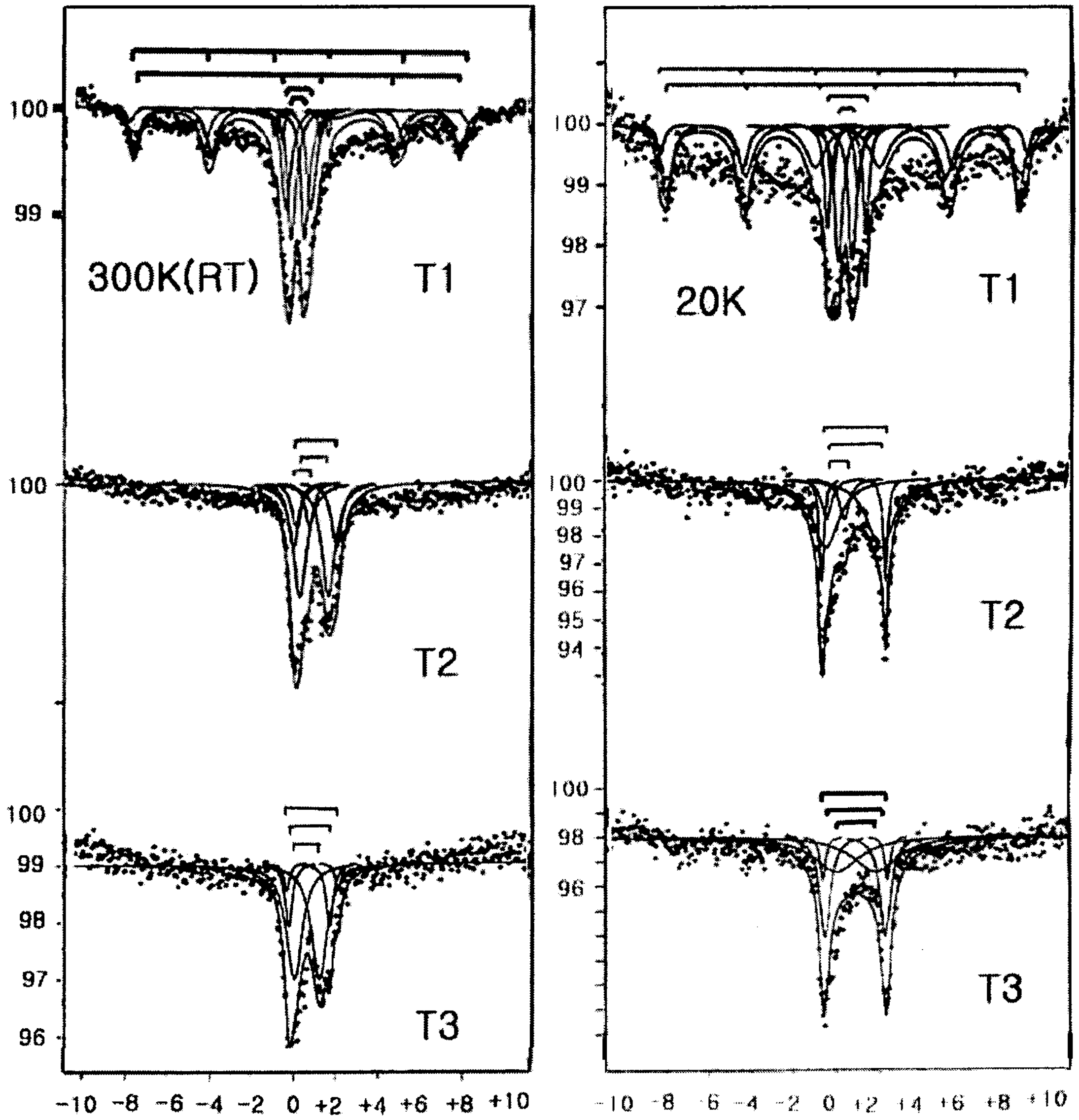

Fig 3 . The spectra of pantiles at 300 K and 20 K

3) Magnetic hyperfine field

Magnetic hyperfine field length from Mössbauer spectrum about plain coarse pottery and pantiles samples in 5 region s can be calculated from 475.282 KOe to 496.486 KOe. And magnetic hyperfine field length for hematites is calculated a scope from 475.282 KOe to 496.486 KOe. In 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 like in case of I. S. and Q. S. length therefore more consistent and variable study on produced time of pantiles , their sorts etc.

Magnetic hyperfine field length of goethite, contained in pantiles samples excavated, in 300K is less than 505 KOe obtained magnetic hyperfine field length of pure goethite. The phenomenon is the same for an opinion of Graham(1989)[12], Vanderberghe(1992)[13], Wang(1992)[14] who indicated that magnetic hyperfine field length of in soil which goethite and hematites in soil is normally less than synthetic goethite magnetic hyperfine field length.

The reason for this fact that magnetic hyperfine field length of goethite, contained in pantiles samples excavated, is less than synthetic goethite magnetic hyperfine field length, shows that disintegration of inner magnetic order, created by partial substitution of diamagnetic positive ion containing Fe^{3+}(ion diameter 0.51 Å) and Al^{3+} (ion diameter 0.51 Å) in goethite lattice, effects on magnetic hyperfine splitting. This fact is proved by the result of Mössbauer spectrum experiment that as amount of diamagnetic Al^{3+}, in goethite and hematites synthetic by substituting Al, is increased their magnetic hyperfine field length is linearly decreased. [15]

Namely structural iron(Fe^{3+} and Fe^{2+}) in normal soil do not exist as independent oxide but exist as material substituted for positive ion like Al^{3+}, Si^{4+} which has similar coordination number in the crystal structure of clay mineral. So it can be estimated that if they were heated, plain coarse pottery and pantiles from clay have change in crystal structure then Fe ions of them also have changes in bond.

Table 2. M ssbauer parameters of cheju plain coarse pottery and pantiles in 5 regions at 300K and 20K

Sam-ple NO	Temp-erature (K)	Fe^{3+} doublet		Fe^{3+} doublet		Fe^{3+} doublet		Fe^{3+} doublet		Goethite			Hematite		
		I.S.	Q.S.	I.S.	Q.S.	I.S.	Q.S.	I.S.	Q.S.	I.S.	Q.S.	Hhf	I.S.	Q.S.	Hhf
		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								

Ⅳ. Conclusion

Through diagnosis of X-ray fluorescence analysis and Mössbauer spectrum in 300 K and 20 K, plain coarse pottery at 5 regions used in this study have very low FeO_3 content as compared with that known in research for clay of volcanic ash of Cheju Island and have higher SiO_2 content, lower AlO_2 content. From this result, it is thought that samples of plain coarse pottery and pantiles in those 5 regions are not made from basalt, containing high iron inclusion old soil mineral content but from partially neutral volcanic rock like trachyte and the iron ion are estimated almost Fe^{3+}, the fact that magnetic hyperfine field length of goethite, contained in pantiles samples excavated, is less than synthetic goethite magnetic hyperfine field length has suggested that disintegration of inner magnetic order, created by partial substitution of diamagnetic positive ion containing Fe^{3+}(ion diameter 0.51 Å) and Al^{3+} (ion diameter 0.51 Å) in goethite lattice, effects on magnetic hyperfine splitting.

And finally it is required to variable study about the uniqueness revealed in T2, T3.

※ Thanks for

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