

Black tea stain formed on the surface of teacups and pots. Part 1 – Study on the chemical composition and structure

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Received 20 June 2005; received in revised form 23 May 2006; accepted 23 May 2006

Abstract

Repeated use of teacups and teapots results in stains that are difficult to remove with normal dish-washing detergent and a soft sponge. The tea scum and tea cream formed in black tea infusion have been investigated previously. On the other hand, the composition and the formation mechanism of the stain are not well understood. The present study deals with phenomena occurring on the surface of porcelain tiles that were immersed in tea infusion brewed with Tokyo tap water. The stain was generated on the tile surface with the lowering of the waterline caused by natural evaporation. The FT-IR spectrum of the stain differed from that of the adsorbed materials below the waterline of the infusion, and the latter was easily removed by pouring distilled water. SEM-EDS analysis revealed the existence of islands of calcium silicates on the underlying organic material, which were probably the oxidative products of polyphenols. Those results suggested that the inorganic ions of calcium and silicate mainly from tap water play key roles together with oxygen in the formation and stabilization of such stains.

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Keywords: Black tea stain; Oxidized polyphenol; Calcium silicate

1. Introduction

Black tea is one of the most popular teas, besides green tea and oolong tea. Tea drinkers and researchers have been taking great interest in its quality and also in its beneficial effects upon human health (Trevisanato & Kim, 2000; Willson & Clifford, 1992; Yang, Chung, Yang, Chhabra, & Lee, 2000; Yang & Landau, 2000). The contents of polyphenols, caffeine and other volatile substances in the tea leaves, the water used for brewing, and its temperature are important factors in determining qualities of tea such as appearance, flavour and astringency (Borse, Rao, Nagalakshmi, & Krishnamurthy, 2002; Jaganyi & Price, 1999; Roberts & Smith, 1963; Schurer, 1960; Scharbert, Holzmann, & Hofmann, 2004; Spiro & Lam, 1995). The beneficial health effects have been attributed to the antioxidant and other

properties of the polyphenolic components, particularly the catechin derivatives (Sava, Yang, Hong, Yang, & Huang, 2001; Su, Leung, Huang, & Chen, 2003).

In hard water areas, an unsightly oily-appearing floating film called tea scum forms on the surface of black tea infusions. Early publications (Spiro & Jaganyi, 1993, 1994a, 1994b; Spiro, Chong, & Jaganyi, 1996; Spiro & Chong, 1996) have been concerned mainly with the relationship between the scum formation and the components involved in tea infusion. Hard water is known to enhance the formation of tea scum, and the contents of caffeine and polyphenols are other key factors in its formation. According to a series of works by Spiro et al., the scum consists of oxidized polyphenols and a few percent calcium carbonate. As a strong aqueous infusion of black tea cools down, it becomes turbid. The coloured precipitate, whose formation causes this turbidity, is known as tea cream (Rutter & Stainsby, 1975). Tea cream is considered to consist mainly of complexes of caffeine with the oxidative products of polyphenols (Roberts, 1963).

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The tea stains that are deposited on teacups and teapots also have a deleterious influence upon the quality. Little attention, however, has been paid to such tea stains, and little is known about them. Once the stain forms on the surface of teacup or teapot and begins to age, it becomes difficult to remove with normal dish-washing detergents. In Japan, green tea has traditionally been drunk, though black tea has recently been gaining in popularity. Some Japanese people consider the tea stain on the teapot used in Japanese tea ceremony to be preferable, and make an effort to create this “seasoned” or “aged” appearance. In this case, just hot water is often used to clean out a teapot. This is generally not the case, however, for black tea stains formed on white teacups, and bleaching or scrubbing is usually needed to remove it. The development of new products for removing the stain without bleaching or physical means has been an important goal for detergent manufacturers. To attain this goal, an understanding of the composition and the structure of the stain is required.

The present paper deals with the phenomena occurring on the surface of porcelain tiles immersed in tea infusion brewed with Tokyo tap water. The setup was intended to simulate actual brewed tea in a teacup. The stain was generated on the porcelain tile surface with the lowering of waterline caused by water evaporation. We investigated the chemical composition and structure of the stain. The stain was characterized by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), Fourier-transform infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy (XPS) techniques. The chemical composition and structure differed from that of the tea infusion itself. The stain was found to consist of oxidized polyphenols together with several percent calcium silicates, instead of calcium carbonate that had been observed in the tea scum formed in hard water. The factors influencing the structural changes and the properties of the stain caused by aging and the addition of chemicals will be studied in the next paper (part 2).

2. Materials and methods

2.1. Preparation of infusion and tea stain

The teabag used was Lipton Yellow Label Tea. Porcelain tiles (SPKO100/L01, 100 × 100 mm) simulating the surface of a teacup were obtained from INAX (Japan), and were used for the generation of tea stains.

In the standard procedure, two teabags were infused at 95 °C for 2 min in 500 ml of pure water or Tokyo tap water in a wide 1-l glass beaker. The Tokyo tap water used in this work was soft water; 0.52 mmol/l of calcium, i.e., 2.91 mg/100 ml CaO, 0.71 mmol/l of magnesium, 0.3 mmol/l of silicate, and 2 mmol/l of carbonate. The pure water contained only a trace of calcium, magnesium, and silicate less than 0.01 mmol/l. The teabag was removed, then a porcelain tile was immersed such that the lower half surface was below

the waterline. The uncovered beaker was allowed to stand for 24 h at room temperature. The tile was withdrawn, and the surface was rinsed with distilled water and dried in air. The above standard procedure was repeated a given number of times using the same tile to accumulate a deposit on the tile surface.

2.2. Analysis of tea stain

The growing process of the tea stain on the tile was observed and recorded by VTR. After drying, the tea stain on the tile was characterized by SEM-EDS (S-2380N, HITACHI) and XPS (Quantum 2000, ULVAC-PHI). XPS is an ultra-surface analysis technique, therefore, the composition results are usually different from the data obtained by other techniques; analysis depth is less than 10 nm for XPS, and several μm for SEM-EDS. In addition, the stain was scraped off from the surface of the tile, dried and weighed, then analysed by FTIR (JIR-6000, JEOL), XRF (System 3270E, RIGAKU), XRD (RINT-Ultima, RIGAKU), CHN analyser (MT-3, Yanaco) and O analyser (CHN-0 RAPID, Heraeus).

3. Results

3.1. In situ observation of stain by video camera

The deposit formation in black tea infused with Tokyo tap water was monitored by video camera. A series of video images taken at the same place is shown in Fig. 1. A brown-coloured deposit was generated in the whole area of the tile surface below the waterline. The dark area that increased with time, however, was clearly observed only at the upper position. The dark deposit was remarkably stable, and insoluble in water and in a wide range of organic solvents such as chloroform, acetone, tetrahydrofuran, dimethyl sulfoxide, methyl alcohol and ethyl alcohol, though the light-coloured deposit was easy to remove with distilled water. The dark deposit on the surface of the tile is not likely to be caused simply by the adsorption of the components in tea infusion. Some chemical reactions must occur primarily around the air–water interface. In the present work, therefore, attention has been directed to the dark deposit, which we define as the tea stain in this paper. The stain exposed to air for a long time would be oxidized by air and consequently be stabilized or strengthened, suggesting that one of the driving force for the formation of the stain is an oxidation reaction.

3.2. Elemental analysis by XRF and CHNO analyser

The tea stain was generated on tiles not only in tap water, but also in distilled water, though the amounts and properties varied between them. The stains formed in each type of water were scraped off the tiles and weighed. Over 5 days, 45 mg of the stain developed in the tap water, compared with 27 mg in distilled water, and the latter stain

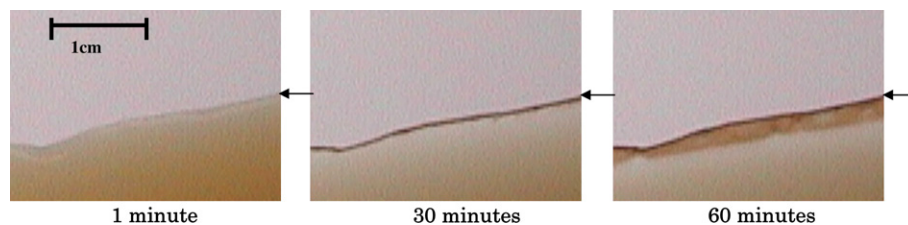


Fig. 1. Video images of tea stain formed on porcelain tiles. Arrows indicate the initial water level.

was relatively easily removed with distilled water. The metallic elements were mainly analysed by XRF, and the results are summarized in Fig. 2. The contents of all detected elements were normalized so that their sum equaled 100%. In both tap water and distilled water, calcium, silicon, sodium and magnesium ions were preferably up-taken into the stains, and potassium remained in the aqueous phase. The presence of those incorporated ions would be crucial for the formation of the stable stain, suggesting the formation of silicates of those cations. The silicates came mainly from the tap water instead of from the tile, because the silicates also formed on the surface of stainless steel, though the data were not shown here. Hereafter in the present work, we focused our attention on the stain formed in tap water. The organic elements were analysed by CHN and O analysers, and results are shown in Table 1. The total amount of those elements was 90.7%, suggesting that the stain was mostly composed of organic materials, though those elements may partly be attributed to the inorganic materials.

3.3. Microstructure analysis by SEM-EDS

A video camera picture and a SEM image with the corresponding EDS elemental distribution maps of the stain are shown in Fig. 3. All those results were taken with the stain on the tile surface. As can be seen from the SEM image, the morphology of the surface of the sample was irregularly shaped, and aggregates or islands were observed. In the EDS maps, the bright points represent the signals from each element in the stain. The EDS results showed that the aggregates contained much more silicon (Si) and oxygen (O), but less carbon (C), and that calcium (Ca) spread all over the surface, suggesting the formation

Table 1

Composition of organic elements of tea stain formed in tap water in a week, determined by CHON analyser (wt%)

C	H	O	N	Total
43.7	4.7	38.3	4.0	90.7

of calcium silicate-aggregates on the calcium-containing organic materials. Small particles with diameter of 5 μm or less were also visible as high-concentration spots of calcium on the EDS maps, but those particles could not be identified.

3.4. Crystal structure analysis by XRD

Indirect evidence for the formation of calcium silicates was shown by SEM-EDS analysis, then XRD analysis was performed to clarify the crystal structure of the material. The XRD pattern of the scraped stain is shown in Fig. 4. A curve with broad bump and several sharp peaks was observed. Those peaks, however, could not be assigned to any kinds of silicates presumed by SEM-EDS and other substances. The amorphous components are probably high molecular weight organic materials such as polyphenols together with small amounts of silicates.

3.5. FT-IR analysis

The IR spectra of the stain, the deposit formed below water line and reference materials such as catechin and calcium silicate were recorded for the 800–4000 cm^{-1} spectral region, as shown in Fig. 5. The spectrum of catechin was characteristic of typical polyphenols, showing the existence of OH in the regions of around 3300–3500 cm^{-1} and 1350 cm^{-1} , C=C at 1450–1600 cm^{-1} , CO at 1200–1300

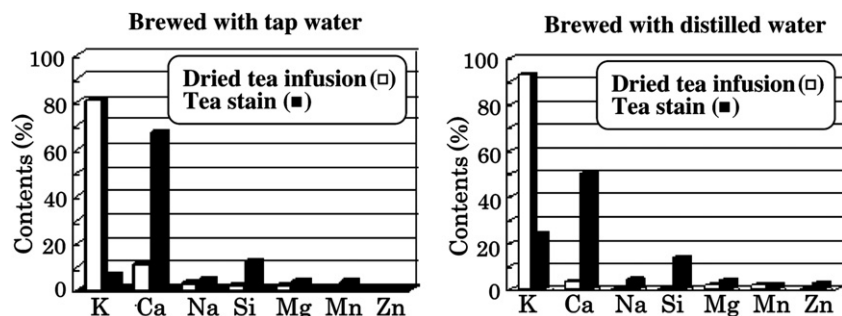


Fig. 2. XRF analysis of metallic elements of dried tea infusion and tea stain formed in tap water and distilled water.

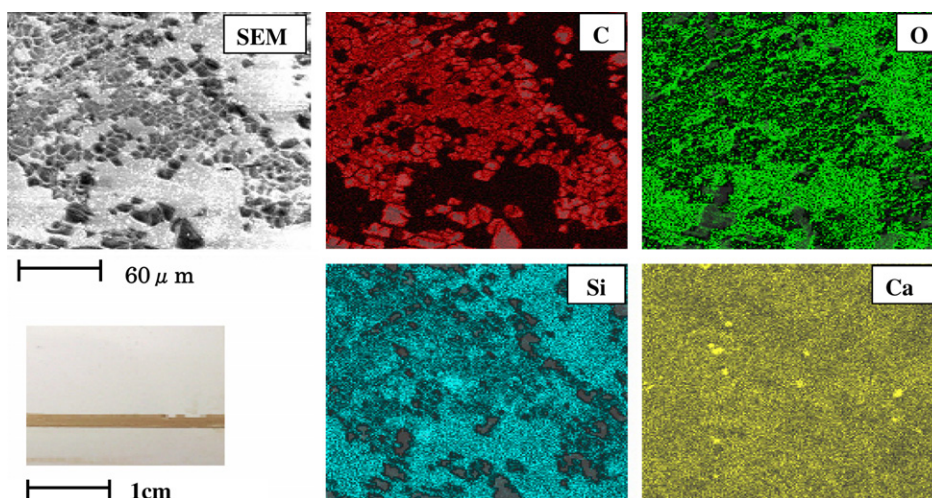


Fig. 3. An optical microscope image of tea stain after 5 days (lower left) and a SEM image (upper left) with corresponding EDS element maps (right).

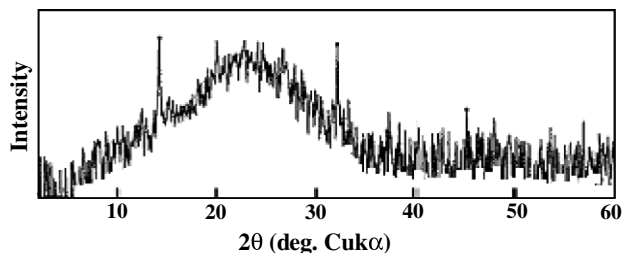


Fig. 4. X-ray diffraction pattern of tea stain.

cm^{-1} , and CH at $1000\text{--}1150\text{ cm}^{-1}$, respectively. The spectrum of the stain was substantially similar to that of catechin, and their spectra were quite different from those of the calcium silicate and deposits formed below the water line. This result would be in accordance with differences in the appearance and solubility observed in the above video monitoring experiment.

3.6. Amino acid analysis

To investigate the contribution of proteins and amino acids to the stain formation, amino acids contained in the tea infusion and in the tea stain were analysed. Total amino acid contents for the dried infusion and the stain were 2.0% and 1.6%, respectively. The amino acid compositions are shown in Table 2. No significant difference was seen between them except for proline contents. Those results suggested that proteins and amino acids are unlikely to play key roles in the stain formation.

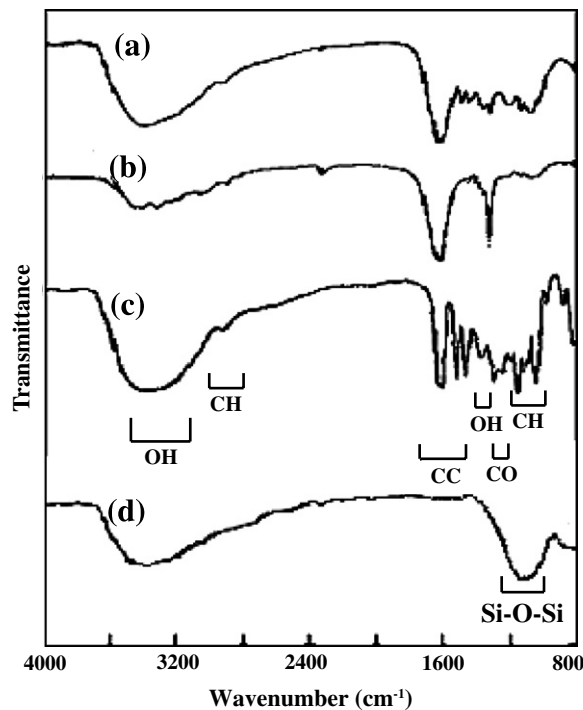


Fig. 5. Infrared spectra of (a) tea stain after 5 days; (b) deposit formed under waterline; (c) standard catechin and (d) calcium silicate.

3.7. XPS analysis

XPS analysis was performed for the stain on the tile, the deposit formed below the waterline and the clean porcelain

Table 2
Amino acid compositions of tea infusion and stain (wt%)

	Asp	Thr	Ser	Glu	Pro	Gly	Ala	Val	Met	Ileu	Tyr	Phe	His	Lys	Arg
Tea infusion	7	3	7	38	10	7	3	3	0	2	4	5	1	1	3
Tea stain	9	2	4	50	3	8	3	3	0	2	2	3	1	2	3

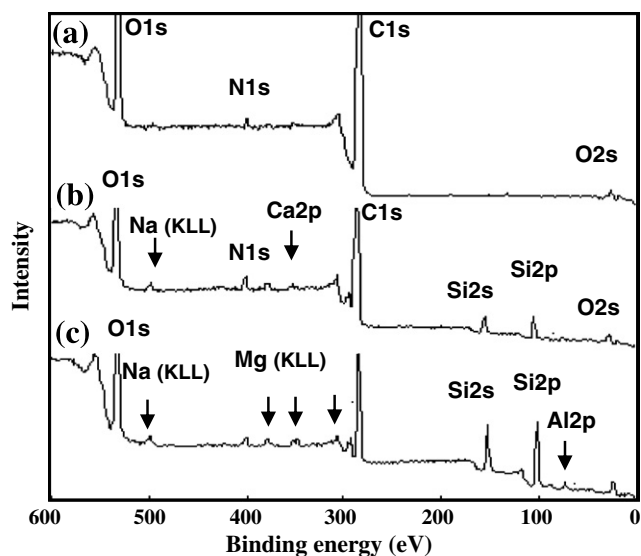


Fig. 6. X-ray photoelectron wide scan spectra of (a) tea stain; (b) adsorbed material under waterline and (c) porcelain tile.

tile. The wide scan spectra and the elemental composition are shown in Fig. 6 and Table 3, respectively. The disagreement of the composition data with the organic element data in Table 1 is due to the difference in the analysis depth between those two techniques. The elements of aluminum (Al), iron (Fe) and sulfur (S) that originate from the tile surface were detected for the deposit formed below the waterline, but not for the stain on the tile. This means that the deposit below the waterline partly or thinly covered the surface of tile, but the stain totally covered the surface. The narrow scan spectra of N 1s, C 1s and Si 2p are shown in Fig. 7. The C 1s line at 284.6 eV attributed to hydrocarbon was used for charge correction. The C 1s shoulder peaks at around 286 eV arose from the carbonyl carbon. The Si 2p binding energy value obtained here for the stain (101.9 eV) agreed with that of the silicates reported previously (Tanizawa & Suzuki, 1995). The N 1s peak at 399.8 eV can be ascribed to amide compounds, probably proteins. No evidence of the silicate formation was given from Ca 2p spectra, because there is generally no significant difference in binding energy values between calcium silicate and calcium carbonate. The combining of this result together with the above SEM-EDS and IR results revealed the existence of calcium silicates on the underlying organic materials that were probably the oxidative products of polyphenols.

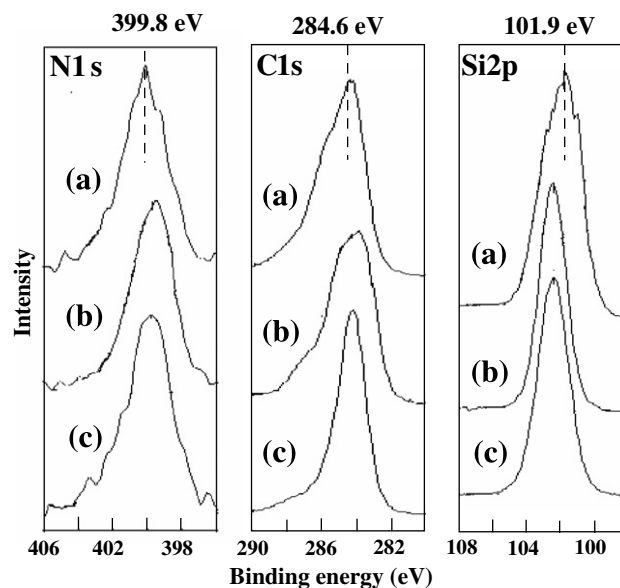


Fig. 7. X-ray photoelectron narrow scan spectra (N 1s, C 1s and Si 2p) of (a) tea stain; (b) adsorbed material under waterline and (c) porcelain tile.

4. Discussion

The black tea contains two major groups of pigments, theaflavins (TFs) and thearubigins (TRs) which are produced by the oxidative polymerization in the fermentation processes (Menet, Sang, Yang, Ho, & Rosen, 2004; Willson & Clifford, 1992). The unsightly coloured tea stain, however, is not simply caused by the adsorption of those pigments from the tea infusion, but by the result of chemical reactions occurring at or around the waterline. The stains consist of organic compounds like the polyphenols and other inorganic compounds. When the stains are exposed to air for too long a time, they are often stabilized and become difficult to remove. One of the driving forces for the formation of the stable stain is probably an oxidation reaction.

Another major factor in stabilizing or strengthening the stain is the formation of silicates covering the underlying organic materials. Previous studies (Spiro & Jaganyi, 1993, 1994a, 1994b; Spiro et al., 1996; Spiro & Chong, 1996) performed using London hard water have shown that the tea scum forming on the surface of a tea infusion consists of oxidized polyphenols and a few percent calcium carbonate. In the present work performed using Tokyo soft water, calcium silicates were detected in the stain instead of

Table 3
XPS surface analysis of stain, deposit and tile (atomic %)

	C	O	N	Si	Ca	P	Mg	Na	Al	Fe	S
Dark coloured stain	71.6	25.4	1.6	0.5	0.2	0.2	0.2	0.1	0	0	0
Deposit below waterline	54.5	36.2	25	4.7	0.3	0.1	0.4	0.4	0.5	0.1	0.2
Porcelain tile	33.4	43.6	1.4	16.4	0.7	0	0.4	0.4	2.6	0.6	0.4

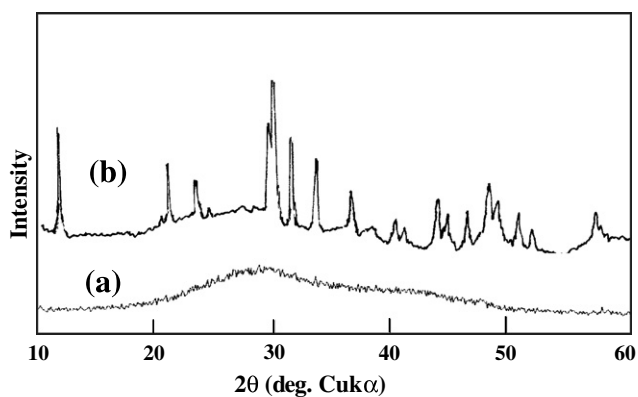


Fig. 8. X-ray diffraction pattern of kitchen sink scale formed in (a) 3 months and (b) 5 years.

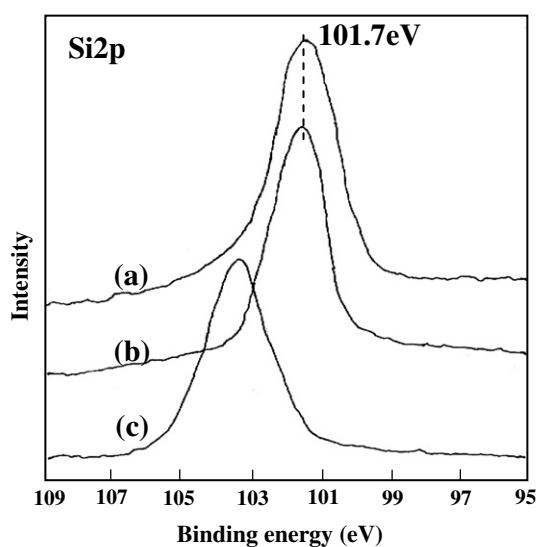


Fig. 9. X-ray photoelectron narrow scan spectra (Si 2p) of (a) kitchen sink scale; (b) tobermorite and (c) silica.

calcium carbonate. We have found that calcium silicates are one of the components in the deposit formed on stainless steel surface known as the kitchen sink scale. The XRD patterns of 3-month and 5-year-old kitchen sink scale are shown in Fig. 8. An amorphous phase was detected for 3-month-scale, and calcium carbonate in calcite type in addition to amorphous phase for 5-year-scale. The formation of calcium carbonate in Tokyo soft water could be explained by the use of alkaline detergents that absorb carbon dioxide in the air to enhance the reaction of calcium with carbonate ions. In Fig. 9, the XPS narrow scan spectra of Si2p for the kitchen sink scale, tobermorite as a kind of calcium silicate and silica are shown as reference materials. The XPS spectra reveal that chemical state of the silicon in the sink scale is close to that of tobermorite instead of silica (Tanizawa & Suzuki, 1995), and that the amorphous phase detected above by XRD is a calcium silicate. Probably the generation of the silicates in the tea stain is also a similar phenomenon, though the underlying oxidized polyphenols coexist only in the tea stain.

Divalent or trivalent cations are known to polymerize organic compounds like protein and saccharides in terms of metal ion-bridging. In fact, we have reported that the oral pellicle and plaque formed on the teeth in oral cavity were accumulated by calcium bridging between specific proteins (Tanizawa, Johna, Yamamoto, & Nishikawa, 2004). To investigate the possibility of calcium bridging in the tea stain, Ca/Si molar ratios were calculated using XPS data: 5.0 for the tea stain formed in 1 day, 1.66 for the kitchen sink scale formed in 1 year and 0.8 for tobermorite. The extremely high value for the tea stain probably suggests that the calcium does not derive only from calcium silicates, but also from the calcium-binding polyphenols.

Tea stains arise largely from the oxidation of tea polyphenolic constituents and from the calcium bridging occurring around the waterline of the tea infusion. Both the oxidation and the calcium bridging are chemically and structurally complex, and their combination is even more so. Here, we have not investigated these phenomena in detail; we will do so in the next paper (part 2).

5. Conclusion

This study dealt with phenomena occurring on the surface of porcelain tiles that were immersed in black tea infusion brewed with Tokyo tap water. The stain forms on the tile surface with the lowering of waterline. Its chemical composition and structure differ from that of the tea infusion itself. The stain consists of oxidized polyphenols together with several percent calcium silicates. The islands of calcium silicates cover over the underlying organic materials to stabilize the stain. Furthermore, both oxidation and the calcium bridging are other major factors in strengthening the stain.

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