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THE FORMATION OF MAGNESIUM-AMMONIUM-PHOSPHATE CRYSTALS IN CANNED SEA FOODS

VIII. The formation of the crystals during the processing of the cans

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I. The amount of the chemical components, Mg and PO_4, which dissolved into boiling water

In the previous paper I[1], the amounts of magnesium and phosphate which were present in various kind of canned foods, were discussed. It is known with certainty that the process of boiling crab meat considerably influences the quality of the canned crab. For example, the quality of water used for boiling, or the boiling time influence the color and elasticity of the meat and the generation of blue meat of canned crab meat. The fact that water used for boiling has intimate relation to the crystallization of struvite in canned crab is understood from the experience that many pieces of struvite (visible or microscopical) generate in canned foods which were processed by sea water. In order to ascertain the amounts of Mg and PO_4 dissolved into the boiling water from the crab meat during the boiling process, the following experiments were performed.

1. Dissolving amounts of Mg and PO_4 in new and old boiling water used in preparation of crab meat

In many crab canneries, sea water is sucked up by a pump and is used for the boiling of crab meat. The removed crab leg meat with the crust from the carapace is heated in the sea water for 20 minutes. The same boiling water is used three or four times without changing. The water becomes dirty from the dissolving of the chemical components. The authors have estimated the difference of the amounts of Mg and PO_4 in the boiling water in accordance with the difference of number of times of use of the boiling water.

1) *Experimental method*

Each 200 *cc* of sea water which was newly sucked up and once used for the boiling and which was used successively three times for the boiling of crab meat, was taken, and 20 *cc* of nitric acid and 2 *cc* of hydrochloric acid were added and hydrolyzed. The hydrolyzates were diluted to 50 *cc*. Twenty cc of the diluted solution was changed to oxine compounds by the method described in paper II[2]. The amount of PO_4 was determined by the method described in American Official Agricultural Chemistry[3].

2) *Experimental results*

The amounts of Mg and PO_4 which were determined and compared in the water once used or three times used for the boiling of crab meat are shown in Table 1.

As seen in Table 1, the greater the number of times of use is, the larger are the amounts of Mg and PO_4 dissolved into the boiling water.

Table 1. Dissolving amounts of Mg and P_2O_5 in new and old boiling water

	New boiling water	Old boiling water
The amounts of Mg (%)	0.00049	0.00079
The amounts of P_2O_5 (%)	0.00074	0.0019

2. The amounts of Mg and PO_4 dissolved in various kinds of water

The authors have determined the amounts of Mg and PO_4 dissolved in fresh water, sea water and various salts solutions used in the boiling of crab meat.

1) Experimental method

The leg with crust of crab which was caught off Nemuro in Hokkaido and removed from the carapace was brought in a thermos container to the laboratory. Ten gram portions of the leg meat were boiled in distilled water, sea water, N/10 $BaCl_2$ and N/10 $CaCl_2$ solutions respectively for 19 minutes. After the boiling, the amounts of Mg and PO_4 were determined in the filtered water from which the meat had been removed.

2) Experimental results

The results obtained by the above described proceeding are shown in Table 2.

Table 2. The amounts of Mg and P_2O_5 dissolved into various kinds of boiling water

Kinds of boiling water / Dissolving amounts (%)	Dist. water	Sea water	Solution of N/10 $BaCl_2$	Solution of N/10 $CaCl_2$
Mg	0.0028	0.0059	0.0028	0.0028
P_2O_5	0.0109	0.0075	0.0045	0.0033

Note: Amount of Mg in sea water was 0.0027.

As seen in Table 2, the amounts of Mg dissolved into various kinds of solution have no difference by the kind of water of solution used for the boiling. That is to say, the dissolved amount of Mg in every kind of water or solution was about 0.0028%. From the results described in paper I[1], the amout of Mg in crab meat has been known to be 0.106%. By the boiling of crab meat, the loss amount of Mg in the meat was known to be about 26%. The dissolved amount of PO_4 is different with the kind of water or solution for the boiling; the dissolved amount of phosphate was the maximum in distilled water.

The reason for the using of $BaCl_2$ or $CaCl_2$ solutions for the boiling was that phosphate will be precipitated in the meat as Ca or Ba salts, and also to prevent the dissolving of phosphate into the solution. In fact, the amount of PO_4 in the $CaCl_2$ or $BaCl_2$ solutions used for the boiling was small for the reason stated above.

After the boiling in those kinds of water or solutions the quality and the color of crab meat showed no difference by the kinds of water or solutions.

3. The amounts of Mg and PO_4 in the crab meat after boiling in the various kinds of water and salt solutions

1) *Experimental method*

Crab meat boiled in various kinds of water and solution was washed once with distilled water and heated in separate Petri-dishes at 108.4 °C (5 *lbs/inch*^{2}) for 80 minutes. The heated dishes were cooled rapidly in running water; 6~7 *g*. of the heated meat was employed for the determination of the amounts of Mg and PO_4.

2) *Experimental results*

Results obtained are shown in Table 3.

Table 3. The amounts of Mg and P_2O_5 in the crab meat after boiling

Samples	Crab meat after boiling in			
	Dist. water	Sea water	N/10 $BaCl_2$ solution	N/10 $CaCl_2$ solution
Mg (%)	0.012	0.020	0.008	0.008
P_2O_5 (%)	0.050	——	0.079	0.093

As seen in Table 3, when sea water was used for the boiling, the amount of Mg in crab meat was maximum showing about 0.02%. This amount was about twice that in boiled meat heated in other kinds of water and salt solutions.

The amounts of Mg in the blocks of meat which were boiled in distilled water, $BaCl_2$ and $CaCl_2$ solutions were small. There is no difference between the amounts of Mg in meat which was boiled in distilled water and in $BaCl_2$ or $CaCl_2$ solutions.

4. Amounts of Mg and PO_4 in the separated juice from the crab meat boiled in various kinds of water and salt solutions

Determination was made of the amounts of Mg and PO_4 in the separated juice from crab meat heated in various kinds of water and salt solutions at 108.4 °C (5 *lbs/inch*^{2}) as described in the previous article.

1) *Experimental method*

A series of samples employed in Experiments 1, 2, 3, was used. Determination was made of the amounts of Mg and PO_4 in 2~5 *cc* of the samples of the separated juice obtained. The state of the crystals formed in the separated juice was observed.

2) *Experimental results*

Results obtained are shown in Table 4.

Table 4. The amounts of magnesium and phosphate in the juice separated from the boiled crab meat, and the form of the crystals formed in the juice

Sample	The juice which were separated from the boiled crab meat in			
	Dist. water	Sea water	$BaCl_2$ solution	$CaCl_2$ solution
Mg (%)	0.0062	0.012	0.0070	0.0020
P_2O_5 (%)	0.024	0.110	0.018	0.0060
Form of crystals	white flour-like	white flour-like	white flour-like	white flour-like

The amount of Mg in the separated juice from the crab meat boiled in sea water is larger than that in other various kinds of water. The amount of Mg in the crab meat thus boiled was about 0.012%. This amount was twice that in other kinds of water and salt solutions. However, there is no difference between the amounts in the boiling juice when distilled water and $BaCl_2$ were used. The crystals of $MgNH_4PO_4 \cdot 6H_2O$ in every separated juice were white minute flour-like.

Discussion

In order to learn about the transmission of the components of Mg which is a key point for the crystallization of $MgNH_4PO_4 \cdot 6H_2O$ and in order to prevent to the dissolution of the components of Mg and PO_4 into the juice separated during the boiling of crab meat by precipitating of the phosphoric acid as phosphate, various kinds of water and salt solutions were employed for the boiling. By the boiling of the meat in distilled water or $CaCl_2$ solution, the amounts of Mg in the separated juice decreased. The amount of Mg in the juice separated from the meat boiled in sea water is surely more than that in fresh water.

Even if the amount of Mg is small in the separated juice in the latter case, the amount is probably sufficient to form the crystals of $MgNH_4PO_4 \cdot 6H_2O$ as described in papers II[3], III[4] and V[5] of this series. In fact, crystals formed in the juice of the meat boiled in $BaCl_2$ and $CaCl_2$ solutions were white minute flour-like.

The color and the taste of crab meat which was boiled in fresh water became worse. Therefore it is undesirable to boil crab meat in fresh water. That is to say, it is practically better to use sea water rather than to use fresh water which is able passively to prevent the crystallization.

II. Relation between the cooling after the sterilization and the formation of the crystals

In the previous papers of this series[2)6)], the authors have reported their observations of the formation of magnesium-ammonium-phosphate crystals in test tubes and the growth of the separated crystals at various temperatures under microscope. The crystals are easily formed in ranges of temperature both above and below about 50°C as boundary. That is the maximum solubility of the crystal of $MgNH_4PO_4 \cdot 6H_2O$. In this case, above 50 °C amorphous crystals are formed, and below 50 °C crystals having easily observable shape occur.

The authors have observed the relation between the growth of the crystals and the velocity of cooling. In order to determine whether the relation holds in the canned food as well as in the test tube, or not, the authors have estimated the cooling curves after heating process of canned food according to the conditions of the cooling process, and have clarified the relation between the conditions of the cooling process and the formation of crystals.

1. Cooling curves of canned foods after heating process

1) *Experimental method*

Canned foods, crab (half pound, flat), salmon (half pound, flat), tuna in brine (half pound, flat), sardine (half pound, oval), after the heating process were cooled under the following various conditions.

i) Cooled in running city water in a vessel of 6~6.5 *l* —A-cooling method (rapid-cooling). This method is customarily employed in land canneries which have a large amount of water.

ii) Cooled by sprinking with city water in the amount of 6~6.5 *l* for 15~20 minutes. —B-cooling method (medium-cooling). This method is also used mostly in land canneries or on floating canneries.

iii) Cooled by air-blast by electric fun. —C-cooling method (slow-cooling). This method is usually employed in floating canneries which have only a small amount of water available.

The change of the temperature in canned foods during the cooling process was measured by a thermocouple.

2) *Experimental results*

As seen in Figs. 1~4, it is evident that the temperature at the center of various canned foods decreased logarithmically.

Here, for the purpose of comparing the cooling condition in the center of various canned foods which are cooled by C-method for example, the authors have estimated the value of the coefficient of the cooling velocity (n) according to the following equation. The obtained results are shown in Fig. 5 and Table 5.

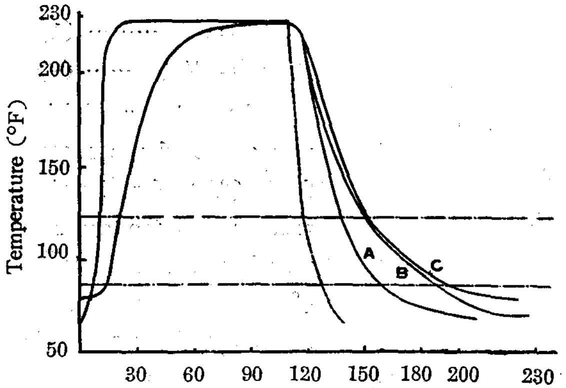

Fig. 1. Cooling curves of canned crab after heating process

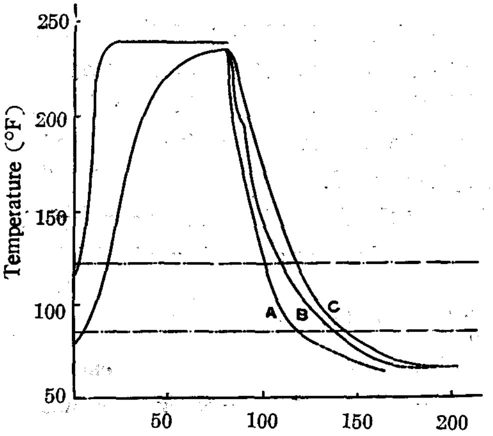

Fig. 2. Cooling curves of canned salmon after heating process

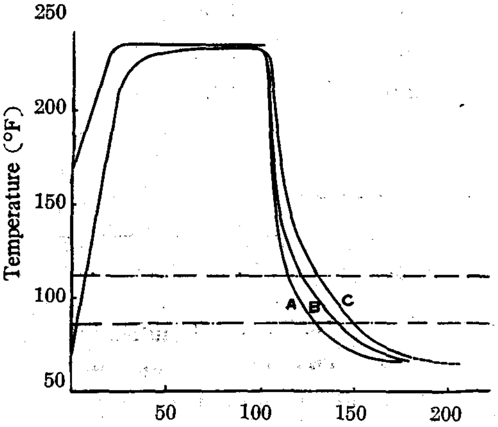

Fig. 3. Cooling curves of canned tuna after heating process

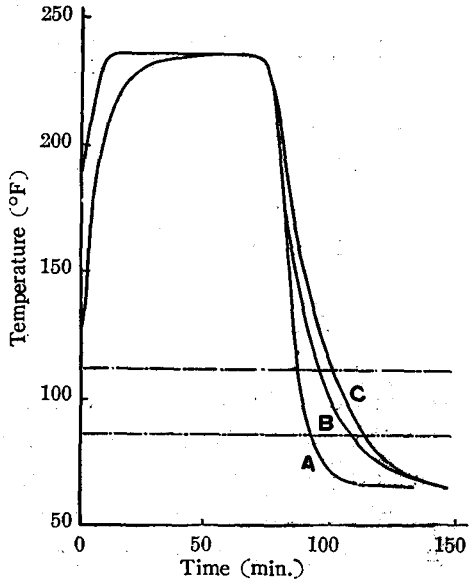

Fig. 4. Cooling curves of canned sardine after heating process

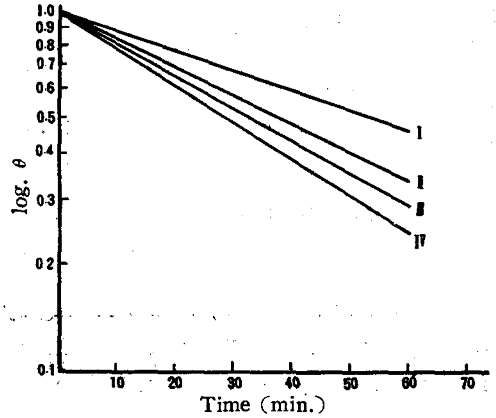

Fig. 5. The value of the coefficient of the cooling velocity of various canned foods

Note: I = canned crab, II = canned salmon, III = canned tuna, IV = canned sardine

Table 5. The values of the coefficient of the cooling velocity of various canned foods

Canned foods	The values of coefficient of the cooling velocity (n)
Canned crab	0.0146
Canned salmon	0.0191
Canned tuna	0.0229
Canned sardine	0.0248

$$\theta = e^{-nt} \quad \cdots\cdots\cdots (1)$$

$$\theta = T/T_0 \quad \cdots\cdots (2)$$

Where T_0 is the initial temperatre of the canned foods (°F) after heating process, T is the temperature in the canned foods (°F) after cooling process, t is the cooling time, n is the coefficient of the cooling velocity of the canned foods.

As seen in Fig. 5, the velocity of cooling of canned sardine is largest, followed in order by canned tuna, canned salmon and canned crab. The heat conductivity of canned crab is worst. It is seen that a long time is required to complete the cooling. From the view point of the difference of the cooling velocity, cooling by C-method may be denominated the slowest, while that by A-method is the most rapid. In the case of cooling by B-method, at the initial period of the process the cooling velocity is as good as by A-method, but in the final period it is like that by C-method.

Here, the time requiring to pass through "**Zone of the formation of large crystals**" described in the previous papers[4)6)] was calculated on cooling curves as shown in Table 6.

Table 6. The time requiring to pass through "Zone of the formation of the large crystals"

Kinds of canned foods	A-cooling	B-cooling	C-cooling
Canned crab	20.0 (min.)	38.0 (min.)	45.5 (min.)
Canned salmon	17.0	28.0	26.0
Canned tuna	18.5	25.0	26.0
Canned sardine	7.0	18.0	17.0

As seen in Table 6, in the cooling by A-method, the time during which the cooling curve passes through "**Zone of the formation of large crystals**" is the shortest. But, in the cooling by C-method, the time is the longest, so the crystals formed are considered to be large and to grow until they become large ones. These facts as actually observed in the canned crab and canned salmon will be described in the next article of this paper.

2. The formation of the crystals in the course of cooling canned crab by the various methods

1) Sample

The legs of crab caught off Nemuro, Hokkaido were removed from the carapace, and boiled with crust in sea water. The meat was taken from the crust, packed in cans, seamed, and then sterilized. After sterilization, the sample cans were cooled by A-method (rapid cooling), B-method (medium cooling) and C-method (slow cooling). The cooled cans were brought to the laboratory and opened after 50 days' storage at room temperature for observation of the states of the crystals formed.

2) Experimental method

Each part, juice, meat and parchment paper, in the canned crab was separated after opening the can. The size and number of the crystals formed in 0.5 *cc* of the juice were estimated on a Thoma's haemacytometer under the microscope. The state of juice of the canned crab was transparent or semitransparent and slight rough, so the crystals in the juice were easily identified by the method described above.

The viscosity of the juice, the amounts of volatile basic nitrogen, total nitrogen, soluble magnesium and phosphate in the juice were estimated by the method described later. On the other hand, the size of the crystals formed on the parchment paper was observed by a low power microscope.

The determination of the viscosity was made by Ostwald's viscosimeter, the determination of the amount of the soluble magnesium was done by the oxine method(1), and the estimation of the amount of volatile basic nitrogen or total nitrogen was carried out by the usual method.

3) Experimental results

Results obtained are shown in Table 7.

As seen in Table 7, the size of the crystals both those formed in the juice and on the parchment paper was small and microscopical, but the number was large in the rapidly cooled cans. The size of the crystals was somewhat larger and the number was somewhat less in the slowly cooled cans. In the case of the slowly cooled cans, few but larger crystals were formed on the parchment paper.

3. The formation of the crystals in the course of cooling of canned salmon by various methods

1) Sample

Some fresh salmon of which the mean body weight was 2,580 *g* and the mean body length was 59.5 *cm* was employed as the material for preparing the canned salmon. The material was packed in cans, seamed and sterilized as usual. After sterilization, some cans were rapidly cooled in water in which ice blocks were put, for 20 minutes;

other cans were cooled most slowly at the temperature at 25 °C. The changes of the temperature in the cans are shown in Table 8.

Table 8. Change of temperature at the center of cans which were cooled by various cooling velocity

Cooling time	Rapid cooling	Slow cooling
0 (min.)	91.5°C	91.5°C
1	66.0	91.0
3	52.0	90.0
5	43.0	88.2
10	33.5	84.2
12	29.5	——
15	26.0	81.0
20	19.0	77.5
60	——	55.1

2) Experimental method

The macrocrystals formed in the canned salmon are generally smaller and fewer than those formed in the canned crab as shown in the previous paper[1].

So the size and the number of the crystals were estimated for visible macrocrystals contained in a can of canned salmon by the method shown in Fig. 6 from

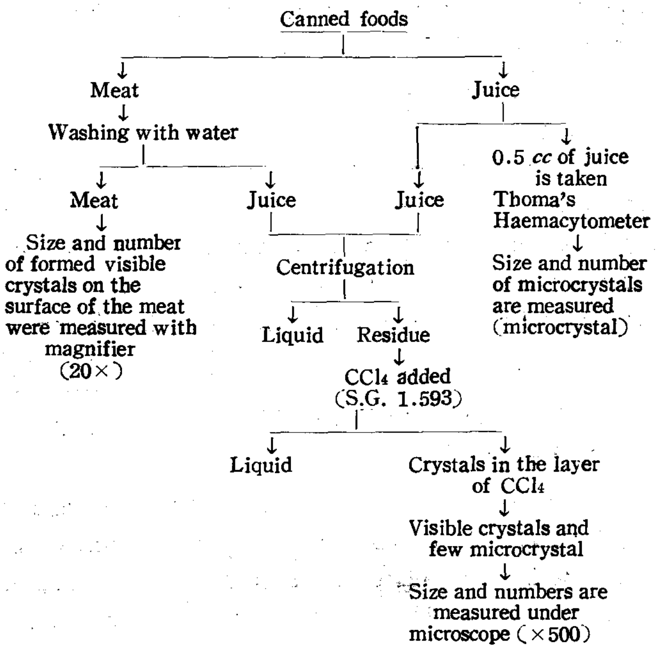

Table 7. The state of the crystals formed in the course of cooling canned crab by various method

Sample cooling method	States of juice					Crystals in juice			Crystals on pearchment paper		
	Viscosity (η/η_0)	V. B. N. (*mg%*)	Tot. -N. (%)	Amount of soluble Mg. (*mg%*)	Amount of soluble PO_4 (*mg%*)	Size (μ)	Number (per cc)	Form	Top (μ)	Side wall (μ)	Bottom (μ)
Rapid cooling	2.3	38.2	1.34	3.0	59	20×25	8×10^4	E	none	none	38×6
Medium cooling	2.3	31.5	1.36	3.4	43	31×15	3×10^4	C	none	57×25	40×25
Slow cooling	2.1	20.0	1.21	6.3	—	72×12	4×10^4	C	300×100	300×100	250×100～ 2000×1000

Note: E=amorphous crystal C=columnar crystal

Table 9. The state of the crystals formed in the course of cooling canned salmon by various method

Cooling method	Sample No.	Crystal in juice							Crystal on meat	
		pH	Amorphous		Microcrystal		Visible crystal		Visible crystal	
			Size (μ)	Number (/*cc*)	Size (μ)	Number (/can)	Size (μ)	Number (/*cc*)	Size (μ)	Number (/*cc*)
Very rapid cooling	1	6.2	16×16	many	25～65×8	5×10⁴	450～1800×250～410	80	250～1800×32～410	85
	2	6.4	16～32×16	many	25～57×8～13	7×10⁴	430～1550×250～490	60	450～1630×200～500	29
	3	6.4	49×16	many	——	none	450～5500×200～300	25	1000～5500×200～1500	7
Very slow cooling	1	6.2	16×16	few	50～110×13～25	3×10⁴	450～5500×300×1000	56	500～6500×200～1800	77
	2	6.2	16×16	few	49～450×13×180	2×10⁴	500～2460×170～570	25	500～2840×200～500	24
	3	6.1	32×16	few	49～100×12～16	7×10⁴	2000～8000×1000～2000	8	——	none

the commercial point of view. For the observation of the state of the microscopic crystals in the juice, 0.5 *cc* of the juice was taken and the size and the shape of the microcrystals were estimated by Thoma's haemacytometer. Then the number of crystals was calculated to the number per 1 *cc* of the juice.

3) *Experimental results*

The observed state of the formation of the crystals during processes of cooling canned salmon by various methods is shown in Table 9.

As seen in Table 9, the size of the crystals either formed in the juice or on the meat was smaller, while the number was larger in the rapidly cooled cans than in the slowly cooled cans.

Discussion

As seen in the results obtained in this experiment either in the canned crab or in the canned salmon rapidly cooled after sterilization, the size of the formed crystals was smaller and the number was greater, but the size of the formed crystals was larger and the number was less in the slowly cooled cans.

These facts agree with the experimental results on the growing of the crystals in the test tubes and with the observed results on the growing of the crystals in the test tubes and with the observed results on the formation of the separaped crystals under microscope reported in the previous paper[8]. In the process of cooling after the sterilization in practical canning, it is evident that the amorphous crystals began to form at 70° ～ 50 °C due to the reaction among each of the components (Mg, NH_4, PO_4) of the crystals. It is considered that crystals of the regular form are scarcely formed above 50°C, because at near 50°C the solubility of the crystal is maximum, and the stabilization of the supersaturated solution will result from the presence of high molecular substances (*e.g.* protein). This fact that the regular crystals are scarcely formed above 50 °C was practically seen during the process of cooling of canned crab by the microscopical observation of the crystals in the juice of the can at 60 °C taken onto the slide glass on which was a small hot water tank as shown in Fig. 1[6]. In the further progress of the reduction of temperature by cooling, when the temperature of the canned foods falls slowly in the range of 50° ~ 30°C which has been called **"Zone of the formation of large crystals"** in the previous paper[2], the larger and the more regular crystals are formed and further grow to the larger ones. On the contrary, when the canned foods are cooled rapidly passing through the 50° ~ 30°C range of temperature in a short time, the crystals will have no reserve to grow to become the large crystals, therefore many small crystals will be formed. The similar formation of the larger crystals is considered to occur during the storing of canned foods in the same range of temepratur. So, the storing temperature should be kept below that of **"Zone of the formation of the large crystals"**, that is to say, should be kept below 20 °C.

III. Relation between the formation of the crystals and the freshness of the raw material

Whether the difference in the formation of the crystal may be caused by freshness of the raw material, or not has attracted much discussion. According to Matsuike *et al.*[7], no difference in the formation of the crystals was observed which could be attributed to the freshness. But, Nagai[8] said that the better the freshness of the raw material was, the more were the crystals formed in canned foods. Also, according to the recent report of Yamada and Fujii[9], the size of the crystals formed in canned crab which was made from unfresh raw meat was small and their number was few.

The authors have studied the relation between the formation of the crystals and the freshness of the raw material.

1. In the case of canned crab

1) Sample

Each sample of canned crab was prepared either from fresh material (volatile basic nitrogen was about 7 *mg%*) which was caught off Nemuro and was soon dealt with after landing, or from unfresh material which was left at room temperature for 2.5 days (volatile basic nitrogen was about 40 *mg%*) after landing. After usual sterilization, the cooling was done at rapid or slow velocities. The cans were brought to the laboratory and opened after keeping at 10° ~ 15°C for 50 days.

2) Experimental method

Experimental method was the same as that described in the previous article.

3) *Experimental results*

The obtained results are shown in Table 10.

As seen in Table 10, no remarkable difference in the state of the formation of the crystal was observed. However, the crystals formed in the juice of the cans prepared from unfresh raw material were larger than these from fresh raw material. On the contrary, the crystals formed on the parchment paper in the former ones were smaller than the crystals in the later ones.

Table 10. States of the formation of crystal in canned crab which were prepared from the raw material of various freshness

Cooling method	Freshness of material	States of juice						Crystals on perchment		
		Viscosity (η/η_0)	Soluble Mg (*mg%*)	Soluble PO_4 (*mg%*)	Crystal in juice			Top (μ)	Side wall (μ)	Bottom (μ)
					Size (μ)	Number (*/cc*)	Form			
Rapid cooling	Fresh	2.2	3.0	59	20×25	8×10^4	E C	none	none	38×6
	Unfresh	2.3	2.4	52	38×8	24×10^3	E C	none	11×4	16×8
Slow cooling	Fresh	2.2	3.4	42	31×15	31×10^4	C E	none	57×25	40×25
	Unfresh	2.0	2.5	43	38×9	25×10^6	C E	38×25	38×25	25×8

Note: E=amorphous crystal, C=columnar crystal

2. In the case of canned salmon

1) *Sample and method*

On a floating cannery, some canned salmon was prepared either from fresh material of half bodies which was promptly dealt with after catching, or from unfresh material of the other half bodies, which was left at the temperature of 17 °C for 28 hours after catching. After usual sterilization, the cans were slowly cooled with showering. The cans were brought to the laboratory and left at room temperature for 70 days and then opened. Experimental method was the same as that described in the previous article.

2) *Experimental results*

The obtained results are shown in Table 11. As seen in Table 11, the number of crystals formed in the cans which were prepared from unfresh material was somewhat less than that in the cans prepared from fresh material, but no remarkable difference in the size of crystals formed in the two types of material was observed.

Discussion

Using canned crab and canned salmon, the authors have observed the relation between the formation of the crystals and the freshness of the raw material. Some difference was observed between cans prepared from fresh and unfresh raw material. The size of

Table 11. State of the formation of crystal in canned salmon which were prepared from the raw material of various freshness

Freshness of raw material	Sample No.	pH	Crystal in juice						Crystal on meat	
			Amorphous		Microcrystal		Visible crystal		Visible crystal	
			Size (μ)	Number	Size (μ)	Number	Size (μ)	Number	Size (μ)	Number
Fresh	1	6.0	16×16	few	48~110×13~25	3×10^4 /cc	450~5500×300~1000	56	500~6500×200~1800	77/can
Unfresh	1	6.2	16×16	few	32~64×16	3×10^4	500~6000×200×800	9	2000~5000×200~1000	10
Fresh	2	6.2	16×16	few	49~450×13~180	2×10^4	500~2460×170~570	28	500~2840×200~590	24
Unfresh	2	6.1	16×16	few	48~110×13	4×10^4	500~3000×200~1000	220	400~3000~×200~800	47
Fresh	3	6.1	16×16	few	32~160×16~96	7×10^4	1000~6000×1000~2000	8		none
Unfresh	3	6.2	16×16	few	48~110×130	2×10^4	1500×800			none
Fresh	4	6.1	16×16	few	32~62×16~32	7×10^4	1000~1500×500	15	2000~3000×1000	2
Unfresh	4	6.2	16×16	few	48×8	2×10^4	500~2000×500	6		none

the visible crystals formed in the canned crab prepared from unfresh meat was smaller than that from fresh raw material, but, no difference in the size of the formed crystals in the canned salmon was observed. Also in comparison with the cans prepared from fresh raw materials, numerous crystals were formed in the cans prepared from unfresh meat. However, as seen in Tables 9 and 10, the state of crystallization was considerably influenced by the velocity of cooling, in comparison with the influence of the freshness of the raw meat. In the cans cooled slowly, the formed crystals were larger in size and less in number, regardless of the freshness of the raw material.

If the conclusion is reached that crystals larger in size and fewer in number are obtained in cans packed with unfresh meat, it will be considered that this occurs owing to the difference of the amount of Mg in the fresh meat and in the unfresh raw meat. In the unfresh meat, the amount of Mg decreases owing to the decomposition and the fragillization of the tissue.

Accordingly, the authors have undertaken to determine the amounts of magnesium contained in canned crab and canned salmon which were prepared from the raw materials of various degrees of freshness. In the canned crab prepared from fresh raw meat, total amount of magnesium was 0.037% and was 0.173% in the anhydrate. But, in the canned crab prepared from unfresh raw material, the amount of magnesium was 0.030% and was 0.151% in the anhydrate. In the canned salmon prepared from fresh or unfresh raw material, total amounts of the magnesium was 0.020% (0.058% in the anhydrate) in the former and 0.011% (0.030% in the anhydrate) in the latter. The obtained results are shown in Table 12.

Table 12. Total amount of magnesium in canned food prepared from the raw material of various freshness

Canned foods		Total amount of Mg (%)	Total amount of Mg in anhydrate (%)
Canned crab	Fresh	0.037	0.173
	Unfresh	0.030	0.151
Canned salmon	Fresh	0.020	0.058
	Unfresh	0.011	0.030

As seen in Table 12, a considerable difference of the total amounts of magnesium was observed between cans prepared from fresh and unfresh raw material. The amount of magnesium contained in the can prepared from fresh meat was more than in that from unfresh raw material. As the tissue of unfresh meat was fragile, the protein was denaturated as noted above. The reduction of the amount of magnesium in the cans prepared from unfresh raw material was considered to be owing to the flowing out during the washing process. Then, the conclusion is that the state of the formation of crystals in the cans prepared from the different freshness of the raw material is considerably influenced by the reduction of the magnesium.

IV. Relation between the formation of the crystals and the difference caused by use of fresh water or sea water for boiling during the processing of canned crab

In the previous article of this paper, the authors have observed that the amount of Mg indicated the largest value both in the crab meat and in the boiling water, in the case of the use of sea water for the processing of canned crab. In this paper the authors report observation on the difference of the formation of the crystal of $MgNH_4PO_4 \cdot 6H_2O$ by the employment of sea water or fresh water.

1) Experimental method

Canned crab was prepared by the usual method. In processing of the can, sea water and fresh water were used for boiling the meat. After the sterilization three cooling methods were used: rapid cooling (A-method), slow cooling (B-method) and very slow cooling (C-method), as described in the previous article. The canned crab thus prepared was brought to the laboratory and opened after 60 days storage. The conditions of the

Table 13. The state of formation of crystal in canned crab which are prepared by using sea water or fresh water for boiling

Boiling water		Fresh water			Sea water		
Cooling method		Rapid cooling	Medium cooling	Slow cooling	Rapid cooling	Medium cooling	Slow cooling
States of meat	Color	discolored	discolored	discolored	good	good	good
	Taste	watery	watery	watery	good	good	good
Viscosity		2.3	2.3	2.1	——	3.1	4.3
V. B. -N. (*mg%*)		38.2	31.5	10.05	31.9	30.2	26.1
Total-N (%)		1.34	1.36	1.46	1.29	1.10	1.21
Soluble Mg (*mg%*)		3.0	3.4	——	3.4	1.7	6.4
Soluble PO_4 (*mg%*)		60	43	——	46	45	——
Crystals in juice	Number	80×10^4 (E) 8×10^4 (C)	100×10^4 (E) 80×10^4 (C)	1000×10^4 40×10^4 (C)	64×10^4 (E) 16×10^4 (C)	80×10^4 (E) 40×10^4 (C)	10×10^4 (C)
	Size (μ)	11×1 (E) 20×25 (C)	16×12 (E) 31×15 (C)	10×3 (E)	9×6 (E) 30×9 (C)	10×12 (E) 50×12 (C)	25×3 (C)
	Form	E C	C	C	E C	E C	C
Crystals of the parchment paper	Top	none	none	300×100	none	none	300×100
	Side wall	none	57×25	300×100	none	190×100	300×100
	Bottom	60×38	40×25	250~2000×100~1000	80×50	200×130	2000×1000

crab meat (color, taste), the viscosity of the juice, the amount of volatile basic nitrogen, total nitrogen, Mg and PO_4 were estimated. The determination of the amounts of Mg and PO_4 was carried out by the method described in previous paper.(2)

2) Experimental results

Results obtained are shown in Table 13.

As seen in Table 13, in the case of the use of fresh water for boiling, the canned crab meat showed light red color as well as discolored, also watery taste lacking in good flavor. On the contrary, when sea water was used for boiling, the meat was beautiful red and had good flavor. In respect to the difference of the formation of the crystal, in the case of use of sea water for boiling, in spite of larger amount of Mg dissolved in the juice of the can, the size, shape and number of the crystals formed in the juice showed no difference from that in the use of fresh water. However remarkable differences of the formation of the crystal were observed with the differences of cooling velocity even in materials prepared with the same kind of water (sea water or fresh water). That is to say, whether in the using of sea water or fresh water for boiling, the more rapidly the cooling was completed, the smaller the size of the crystal was.

Considering from the results obtained, it is better to use sea water for the boiling for the sake of the color and taste, as no difference was seen in the size of the crystals. Rapid cooling after the heating process must be recommended because the size of the crystals keeps small.

Summary

When the various kinds of water and salt solutions were used for boiling, the amount of Mg dissolved was 0.0028%. There is almost no difference in this respect among the kinds of water and salt solutions. The loss amount of Mg in crab meat by boiling was about 26%. The amounts of Mg and PO_4 in crab meat and in the juice separated by boiling were maximum in sea water being twice the values obtained in the use of distilled water and $BaCl_2$ or $CaCl_2$ solution.

The velocity of the cooling of canned foods after heating process is influenced according to the various cooling methods or to the kinds of canned foods. Temperature of the cans falls rapidly in the cooling tank having a large amount of water but when the canned foods are cooled by air-blast by electric fun, the temperature of the cans falls slowly.

If the canned foods are slowly cooled taking a long time to pass through the range of the temperature 50° ~ 30 °C, which is called "**Zone of formation of the large crystal**", the formed crystals are comparatively larger and fewer. But, when the canned foods are cooled rapidly passing through the 50° ~ 30 °C range in a short time, the formed crystals are comparatively smaller in size and more in number.

Thus, it is important to cool canned foods rapidly after the heating process.

In the cans prepared from raw materials of different degrees of freshness the difference between the state of the formation of the crystals was observed to be dependent only upon the difference of freshness of raw material. However, it was observed that the crystals formed in the cans prepared from unfresh raw material were smaller in size and more in number. But, after all the differences caused by degrees of freshness of raw material were less than the difference caused by the various velocities of cooling.

The authors have observed the difference of the formation of the crystals in canned crab which was prepared by using sea water or fresh water and by cooing rapidly or slowly after the heating process. According to the results obtained, when sea water was used for the boiling, the quality of the canned crab becomes better than when fresh water was used.

More remarkable difference of the formation of crystals was influenced by the velocity of the cooling than by the difference in use of the kind of water. Even if fresh water was used for the boiling, the minimum amount of Mg was present sufficient to form the crystal in the juice; therefore sea water should be used, and the product cooled rapidly to prevent growth of crystals to larger size.

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