# Alterations of ceramics due to contact with seawater

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Prolonged immersion in seawater results in chemical alteration of ceramics. This interaction primarily involves some earth alkalis. In the first experiment (six years duration), a powdered calcareous ceramic lost up to one-third of its calcium, gained an equivalent molar proportion of magnesium, and lost some of its strontium. XRD analyses showed it is free calcium phase (CaCO<sub>3</sub>, Ca(OH)<sub>2</sub> or CaO) that disappears, and that Mg<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub> 3H<sub>2</sub>O is formed.

A second experiment, two months of contact with seawater for fired synthetic mixtures of calcite + quartz and calcite + kaolinite, confirmed the previous results for Ca and Mg.

Another series of experiments was carried out on three different clay types fired at 700, 900 and 1100°C. These ceramic materials were then tested in briquette and powder form for periods of three, five, and ten months. Seawater was renewed every two weeks for a part of the experiments. The results obtained showed limited changes in Ca and Mg proportions for less fired samples only. The results did not vary between the briquette and powder samples, nor did renewal of the seawater affect the results. Apparently the duration of contact is the major factor in this phenomenon. Concerning Sr, its behavior depends mainly on the mineralogical nature of the ceramic material and its firing temperature: while the noncalcareous paste loses some of its strontium, the calcareous one adsorbes this element from seawater.

These alteration phenomena are explained by the dissolution of free calcium phases in presence of Mg<sup>++</sup>. This augments the pH in the pores and leads to precipitation of Mg(OH)<sub>2</sub> or Mg<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub> 3H<sub>2</sub>O.

Some of these experiments will continue to run for several years to examine both effects of time and agitation of seawater on these chemical interactions.

KEY-WORDS: archaeometry, alterations, ceramics, earth-alkalis, seawater.

This paper presents a part of an experimental exploratory research work carried out on eventual physico-chemical alterations of archaeological ceramic bodies at different stages of their life: fabrication, use and conservation (Bearat 1990).

In fact, the research works concerning ceramics' alterations due to conservation in marine media are very scarce (Picon 1976; Lemoine et al. 1981).

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In the absence of archaeological samples and in order to understand the role of the different parameters affecting this type of alteration we preferred the empirical approach to these phenomena.

## I. EXPERIMENTS

We carried out three groups of experiments (Table I):

- 1. Calcareous clay fired at 1000°C for 1 h, powdered and kept in contact with unrenewed seawater for about 6 years (3.5 g of powder in 200 ml of seawater).
- 2. Two synthetic mixtures: 1/1 weight of calcite and kaolinite and 1/1 weight of calcite and quartz. Both were fired at 1000°C for 15 h and then kept in unrenewed seawater for 2 months (4 g of powder in 200 ml of seawater).
- 3. Three clay types: natural noncalcareous (NN); same clay to which 20% CaCO; had been added (NC) and a natural calcareous one (SC). Samples of each clay type were then fired at different temperatures: 700°C; 900°C and 1100°C. These samples were experimented in different ways:
  - in form of briquettes (4-6 g) for 6 months in 200 ml of unrenewed seawater for a part and in 100 ml of bimonthly renewed seawater for the other;
  - in form of powder (5 g) for 5 and 10 months in 200 ml of unrenewed seawater for a part and for 3, 5 and 10 months in 100 ml of monthly renewed seawater for the other.

Before analysis, briquettes were brushed and rinsed with demineralized water. Powders were rinsed several times with boiling demineralized water. These samples were analysed chemically and studied in X-ray diffraction.

#### II. RESULTS

TRIAL 1 (Table II):

This calcareous sample fired at 1000°C showed, after 6 years of contact with unrenewed seawater, a loss of 6 wt. % CaO and a gain of 4.5 wt. % MgO. It lost also some of its strontium. The molar fraction of the calcium lost is equal to that of magnesium gained.

XRD analysis showed the presence of the artinite (basic magnesium carbonate: Mg<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub> '3H<sub>2</sub>O), which was absent in the original sample, and the absence of calcite lines which were present in the initial sample.

#### TRIAL 2 (Table III):

Both mixtures: calcite + kaolinite and calcite + quartz fired at 1000°C showed after 2 months of contact with seawater similar behaviour: an important loss in calcium and an equal gain (in molar fraction) in magnesium.

XRD analyses showed the disappearance of the portlandite: Ca(OH)2 as well as the larnite: \(\beta\)-Ca2SiO4, and the appearance of the brucite: Mg(OH)2.

	Trial 1	Tri	al 2		trial 3	
	Calcareous clay n° 1		+	Non calcareous natural clay	Noncalcareous clay + calcite	Calcareous clay n° 2
	(18 % CaO)	50 % (in raw	CaCO <sub>3</sub> mixture)	(0.5 % CaO)	(13 % CaO)	(12 % CaO)
Temperature	1000°C	100	o°C	70	o°C, 900°C, 1100	°C
Firing time	rh	I	5 h		15h	
Material stata in the medium (powder or sherd)	powder	pov	vder		powder & sherd	
Evolution of marin medium	Unrenewed seawater		newed	Renewed	l and unrenewed	seawater
Staytime in seawater	6 years	2 mc	onths	3, 5, 6 and 10	o months (depend	ing on trials)

Table I Brief description of trials

Table II Chemical analysis of a calcareous clay fired at 1000°C then powdered, before and after 6 years of contact with unrenewed seawater. (Results for zero loss on ignition and a summe brought to 100.)

Contact time	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO MgO	Na <sub>2</sub> O	K <sub>2</sub> O	MnO	P <sub>2</sub> O <sub>5</sub>	Ba	St
with seawater	%	%	%	%	0/0	%	%	%	%	ppm	ppm
0	53.5	14.0	6.35	0.69	18.1 3.55	1.03	2.45	0.106	0.22	290	450
6 years	54.4	14.2	6.40	0.74	12,4 8,10	1.03	2.40	0.100	0.28	290	3.70

Table III Evolution of CaO and MgO proportions in two synthetic mixture

Mixture 50%:50%	Contact time (Months)	CaO	MgO
Kaolinite +		38.5	0.2
calcite	2	25.5	9.9
Quartz +		35.0	O. I
calcite	2	17.0	1 1.8

Results for a **~** ed sea , powdered and maintained in ignition. and clays fired a

1 100 390 210 205 215 385 Sr (pppm) 210 225 230 130 3 % 5 180 380 420 440 205 165 165 1100 485 4475 440 440 440 (mdd) temperat Ba Firing 495 495 495 450 365 365 365 1.100 0.67 0.65 0.65 3.20 3.20 %) MgO 700 0.67 0.80 0.80 3.10 3.10 3.10 13.05
13.20 11.95 12.00 0.25 0.30 (%) 13.10 12.80 0.20 0.30 906 CaO 12.90 13.10 0.20 0.30 Stay time ~ ° 1 10 ~ ~ ~ ~ ~ 0 Clay type N

ed and pu

			CaO (%)			(%) Ogu			Ba (ppm)			Sr (ppm)	
Clay type	Stay time	Firing t	eratur		Firing	temperatur	(C) (C) (C) (C)	Firing		(°C)	Firing	temperatu	(C) e
	(months)	400	006	0011	200	006	1100	700	900	1100	200	900	0011
		0.30	0.30	0.30	0.67	0.68	0.67	495	485	485	210	205	205
					0.80	0.80	0.75	495	490	495	105	175	210
		0.25	0.25	0.25	0.85	0.80	0.75	490	\$0\$	490	OII	170	210
		0.20	0.20	0.20	0.8	0.80	0.75	465	455	500	001	165	210
		13.10	13.10	13.05	19.0	0.60	0.60	405	415	415	205	210	210
		13.00	13.20	13.35	0.90	0.70	0.65	415	470	425	<b>591</b>	225	215
		~	13.25	13.65	0.90	0.70	0.70	415	430	430	091	220	215
	01	12.45	12.60	13.05	0.90	0.65	0.60	415	430	430	091	255	250
		06.11	06.11	11.95	3.10	3.15	3.12	365	375	375	380	385	385
		11.55	12.05	12.15	3.30	3.20	3.25	380	375	380	420	390	390
		H	11.70	12.00	3.30	3.20	3.20	370	380	370	430	385	390
		11.25	11.55	12.15	3.15	3.05	3.05	360	370	370	430	385	395

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ij and unpowdered ignition.

			CaO (%)			MgO (%)			Ba (ppm)			Sr (pppm)	
	Stay	Firing	temperatur	(°C)	Firing	ו שַׁ	re (° C)	Firing		(C)	Firing	temperature	
type	time (months)	8	8		200	006		8	8		700	006	0011
Z	9	0.30	0.30	0.30	0.67	0.88	0.67	495	485	485	210	205	205
2 Z	9	13.10	13.20	13.05	0.61	0.60	0.00	405	415	415	205	210	210
<b>S</b> S	9	11.90	11.90	11.95 12.15	3.10	3.15	3.12	365	375	375	380	385	385

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unpowdered and maintained in ignition. and

			CaO (%)			MgO (%)			Ba (pppm)			Sr (ppm)	
Clay	Stay	Firing	temperatur		Firing		re (°C)	Firing	temperatur	(°C)	Firing	ten	
	(months)	90/	006	201	200	006	1100	8	8	8011	90/	006	0011
	9	0.30	0.30	0.30	0.67	0.88	0.67	495	485	485	210	205	205
	9	13.10	13.10	13.05	0.61	0.60	0.60	405	415	415	205	210 225	210
SC	9	11.90 11.45	11.90	11.95	3.11 3.35	3.15	3.12 3.25	365	375	375	380	385	385

#### TRIAL 3

The results of this trial can be divided in four cases according to experimental conditions:

- powdered ceramics in unrenewed seawater (Table IV);
- powdered ceramics in renewed seawater (Table V);
- ceramic briquettes in unrenewed seawater (Table VI);
- ceramic briquettes in renewed seawater (Table VII).

Excluding the case of strontium which will be discussed later and the ceramic briquette SC fired at 700°C, we observe only very weak variations for calcium, magnesium and barium. These variations concern only the samples fired at 700°C.

From these results, as well as those obtained recently on running experiments, it seems that for a contact time less than two years renewing or not the seawater for powders as for briquettes, does not lead to a significant change.

All calcareous samples fired at 700°C showed a thin deposit layer on their surfaces which were analysed by XRD. This deposit is composed of aragonite and calcite.

These results seem surprising if compared to those of both previous trials. Only a briquette sample (SC) fired at 700°C gave results comparable to those of 1st and 2nd trials. But it is difficult to explain the behaviour of this sample if compared to the same sample powdered and examined in the same conditions. However, excluding this case, the fact that there is no difference between powders and briquettes probably indicates a slow process.

## III. DISCUSSION

#### A. CASE OF CALCIUM AND MAGNESIUM

In both calcareous clays (NC and SC), the major part of calcium is present in the form of calcite. This mineral dissociates on firing over 800°C to give CaO which reacts with other constituants. This reaction depends on different factors: firing temperature and atmosphere, chemical and mineralogical nature of the initial clay, calcite granulometry and presence or not of catalysts such as NaCl. Unreacted CaO rehydrates to give Ca(OH)<sub>2</sub> which absorbes slowly CO<sub>2</sub> to give secondary calcite. CaO, Ca(OH)<sub>2</sub> or CaCO<sub>3</sub> can react with surrounding solutions, seawater for instance.

In fact, calcite is much more soluble in seawater than in ordinary water (Harvey 1945). It is also more soluble in presence of Mg<sup>++</sup> (Kuo and Mikkelsen 1979). This solubility can be expressed by the following equilibria:

(1) 
$$CaCO_3 = Ca^{++} + CO_3^{--}$$
  $K_{CaCO_3} = 10^{-8.3}$ 

Hydrolysis of carbonate ions elevates the pH:

(2) 
$$CO_3^{--} + H_2O \leftrightharpoons HCO_3^{-} + OH^{-}$$
  $K_{HCO_3^{-}} = 10^{-10.3}$   
(3)  $HCO_3^{-} + H_2O \leftrightharpoons H_2CO_3 + OH^{-}$   $K_{H2CO_3} = 10^{-6.4}$ 

Decomposition of carbonic acid:

(4) 
$$H_2CO_3 = H_2O + CO_2$$
  $K_{CO_2} = 10^{-1.47}$ 

The solubility of CaCO<sub>3</sub> will be controlled by CO<sub>2</sub> pression in water on one hand and by the pH, which is controlled by an eventual precipitation of OH<sup>-</sup> ions, on the other hand.

But the Mg<sup>++</sup> ions which are very abundant in seawater react with OH<sup>-</sup> ones to give Mg(OH)<sub>2</sub>:

(5) 
$$Mg^{++} + 2OH^{-} = Mg(OH)_{2}$$
  $K_{Mg(OH)_{2}} = 5 \times 10^{-11}$ 

The dissolution of CaCO<sub>3</sub> rises the pH, which results simultaneously in precipitation of Mg(OH)<sub>2</sub> or Mg<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub> '3H<sub>2</sub>O. This is always true for Ca(OH)<sub>2</sub> which is more soluble than CaCO<sub>3</sub>.

Therefore, these reactions explain then the equality between molar fractions of calcium lost and magnesium gained.

Indeed, a marine medium is an open system where CO<sub>2</sub> pression and pH are almost constant, only varying with temperature and depth. But we can say that the pores of a ceramic constitute a somewhat closed system where exchange rate with the surroundings is slower than that of calcite solubility reactions. Therefore, it is here in the pores where we expect to have such alteration phenomenon which depends essentially on the open porosity of the ceramic body.

However, some of these experiments which are still running, as well as some analyses (actually carried out) on archaeological examples, of the same production and coming from both marine and land excavations, will permit better understanding and explanation of this phenomenon.

#### B. CASE OF STRONTIUM

Regarding the results obtained for strontium we observe the following facts:

- 1. These variations are more important in powdered samples than in briquettes.
- 2. The action of seawater is better noted on less fired samples (Figs 1 and 2).
- 3. While the major part of the loss in Sr is observed during the first three months, the gain in this element, for certain samples, progresses slowly (Figs 1 and 2).
- 4. The three clay types do not show the same behaviour (Figs 1 and 2):
  - noncalcareous clay (NN) fired up to 900°C loses some strontium;
  - natural calcareous clay (SC), when fired at 700°C, gains some strontium while fired at 900°C and 1100°C it shows stable content in strontium;
  - the first clay to which 20 wt. % calcite was added (NC) shows an intermediary behaviour: it looses Sr when fired at 700°C (but still less than NN) and it gains some Sr when fired at 900°C and 1100°C;

- the calcareous clay fired at 1000°C and which stayed in contact with seawater for 6 years lost some Sr.

In ceramics, the strontium can be present in two forms: either associated to clay minerals or to CaCO<sub>3</sub>: calcite or aragonite (Kinsmin 1971; Dedek 1966). In the first case, Sr<sup>++</sup> ions are mobile and can be replaced by other smaller ones as Mg<sup>++</sup>, while it is quite stable in the second.

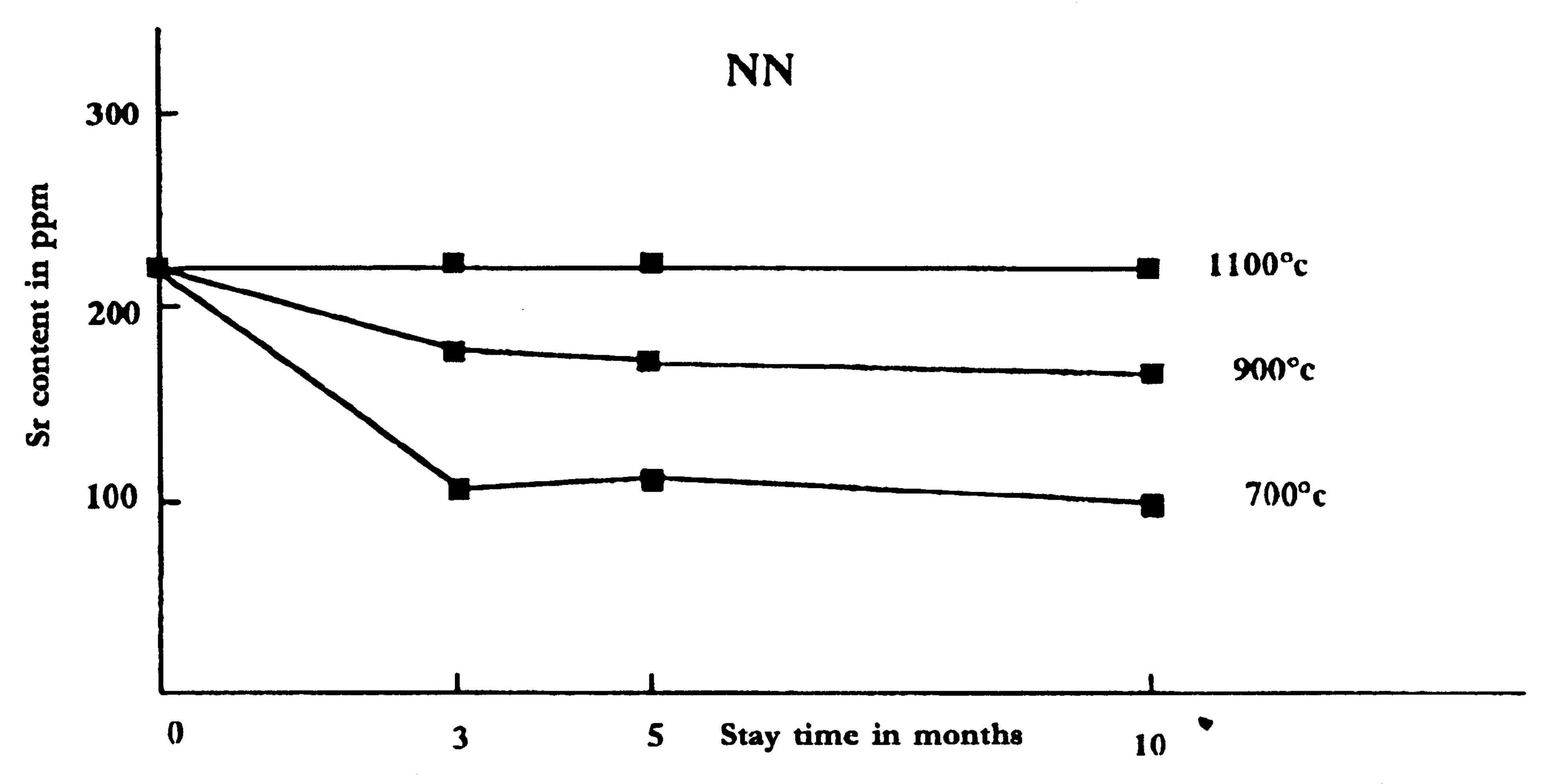


Fig. 1. Sr contents of a non-calcareous clay fired at 700, 900 and 1100°C, powdered after 3,5 and 10 months of contact with monthly renewed seawater.

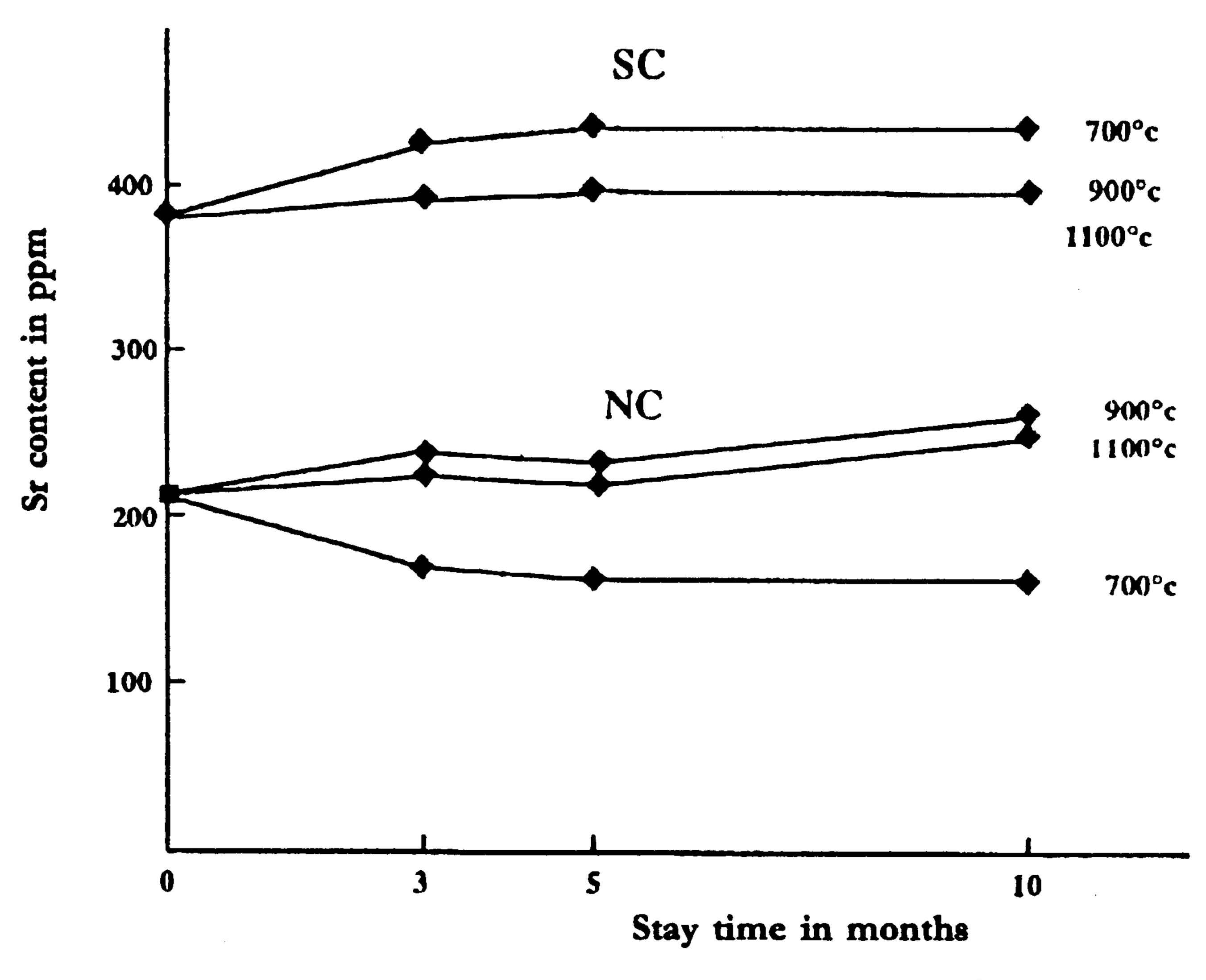


Fig. 2. Sr contents of two calcareous clays fired at 700, 900 and 1100°C, powdered and maintained in monthly renewed seawater for 3, 5 and 10 moths.

In noncalcareous clay (NN), the major part of Sr is probably associated to clay minerals. Given that Mg<sup>++</sup> ions are easily absorbed by these minerals (Monaco 1970), we can then explain the loss of Sr for this clay (NN) in contact with seawater by Sr/Mg ion exchange. At higher firing temperatures, Sr may participate to the development of the glassy phase and becomes less mobile.

For natural calcareous clay (SC) which is richer in Sr, we observe the contrary. Fired at 700°C, this clay tends to uptake strontium. The stability of Sr<sup>++</sup> associated to CaCO3 lattice and the affinity of the latter to absorbe these ions which are abundant in seawater can explain the behaviour of this clay. At higher temperatures, CaCO3 proportion will be diminished and consequently the uptake of Sr decreases.

If we admit these hypotheses, the behaviour of the clay (NC), which reassembles characteristics of both noncalcareous clay (NN) and calcite, becomes explicit. In fact, fired at 700°C this clay (NC) loses some strontium, but still less than (NN) either because both mechanisms proposed previously are active (i.e., absorption of Sr<sup>++</sup> by CaCO<sub>3</sub> and loss of Sr by ion exchange with Mg in clay minerals), or because CaCO3 tends to take these ions (Sr<sup>++</sup>) directly from clay minerals.

The fact that the calcareous clay, fired at 1000°C, lost some strontium after 6 years of contact with seawater, can be explained by the dissolution of calcite which results in a loss of associated Sr.

# IV. CONCLUSIONS

- 1. The ceramic/seawater interactions which concern essentially earth-alkalis, show that the mineralogical nature of the clay and its firing temperature play important roles in the observed phenomena.
- 2. A calcareous ceramic may loose a part of its calcium to gain, in molar fraction, an equal proportion of magnesium. The Ca content, firing temperature and open porosity of this ceramic as well as the rate of renewing seawater in the pores and characteristics of the marine medium (salinity, depth, etc.) are the parameters which control the rate of these reactions (Figs  $_3-4$ ).
- 3. The case of the strontium is somewhat complicated, because free calcium compounds that can fix this element from seawater might be dissolved by this water. There is some competition between these two mechanisms during the first period of immersion, but later, if there will be a complete dissolution of these compounds, we should observe simultaneously a loss in strontium.

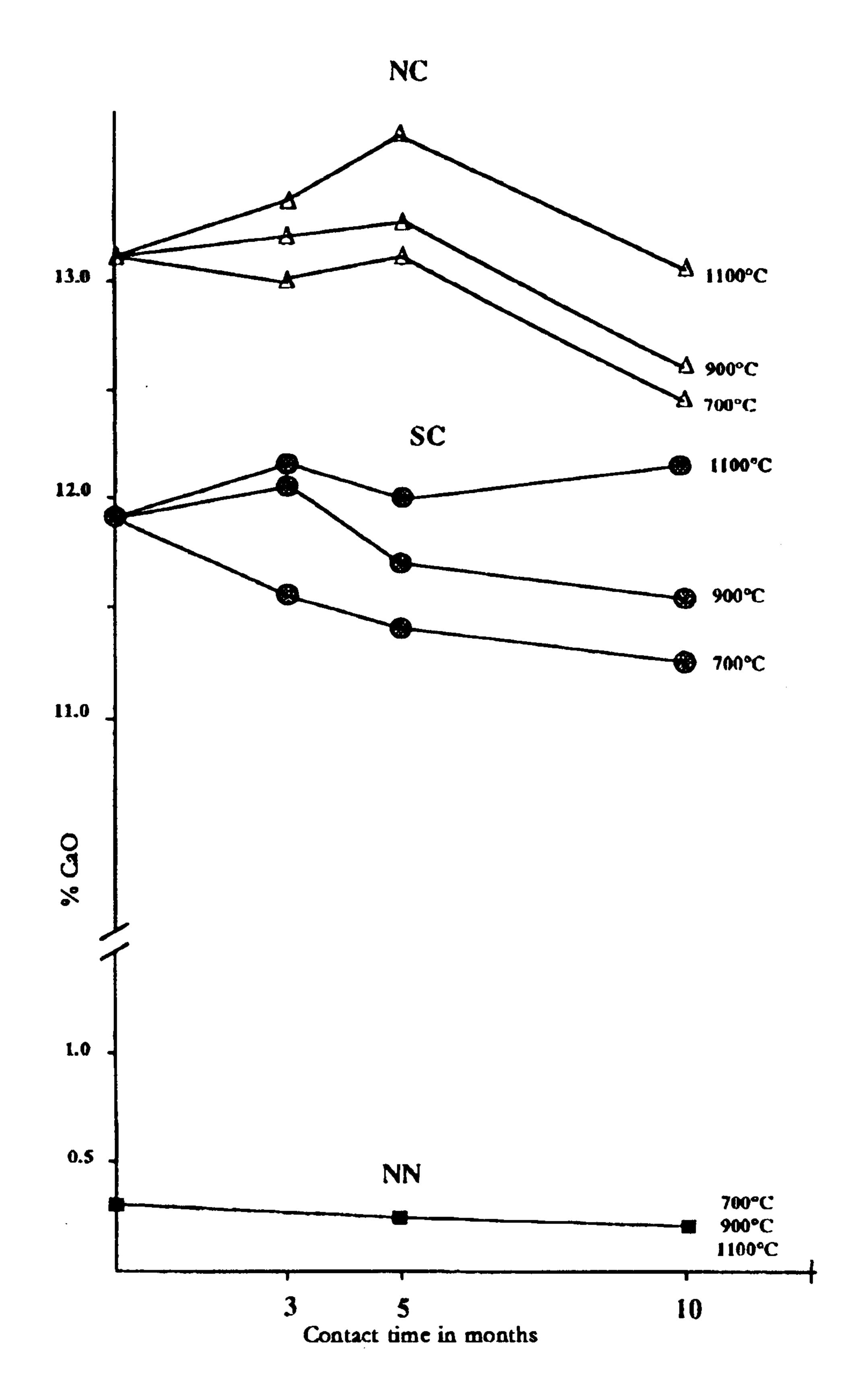


Fig. 3. Calcium contents of three clay types fired at 700, 900 and 1100°C after 3, 5 and 10 months of contact (in form of powders) with monthly renewed seawater.

Fig. 4. Magnesium contents of three clay types fired at 700, 900 and 1100°C after 3, 5 and 10 months of contact (in form of powders) with monthly renewed seawater.

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