

# Laser-induced effects on tooth structure

## VI. X-ray diffraction study of dental enamel exposed to a CO<sub>2</sub> laser

SIRKKA KANTOLA, ENSIO LAINE & TOIVO TARNA

Institute of Dentistry and Department of Physics, University of Turku, Finland

Kantola, S., Laine, E. & Tarna, T. Laser-induced effects on tooth structure. VI. X-ray diffraction study of dental enamel exposed to a CO<sub>2</sub> laser. *Acta Odont. Scand.* 31, 369—379, 1973.

The investigation was carried out in order to study crystallographic alterations in lased dental enamel. By means of X-ray diffraction studies it was proved that laser-induced effects produced recrystallization and growth of crystallite size in the hydroxyapatite crystals of dental enamel. In the X-ray diffraction pattern of an enamel sample after CO<sub>2</sub> laser irradiation a foreign peak for hydroxyapatite structure was seen. Consistently, there should be a small amount of  $\alpha$ -calcium orthophosphate in lased enamel.  $\alpha$ -calcium orthophosphate is the high-temperature form of the apatite phase of tricalcium phosphate.

*Key-words:* Lasers; dental enamel; X-ray diffraction

*Sirkka Kantola, The Institute of Dentistry, University of Turku, Lemminkäisenkatu 2, SF-20520 Turku 52, Finland*

Structural changes produced by a CO<sub>2</sub> laser in dental enamel and dentine were studied with the aid of microradiography and polarized light microscopy in a previous study (Scheinin & Kantola, 1969b). In that context, reference was made to a study (Lobene & Fine, 1966) according to which the X-ray diffraction pattern of lased enamel and unlased enamel proved to be similar. In a later investigation (Lobene *et al.*, 1968) the X-ray diffraction pattern of enamel exposed to CO<sub>2</sub> laser irradiation was compared with that of normal enamel, and it was found that the X-ray diffraction pattern of a powdered enamel sample after CO<sub>2</sub> laser irradiation was essentially the same as that of hydroxyapatite. However, weak foreign lines were seen at 7.62 ångströms, 6.32 Å, 5.74 Å and 3.66 Å. These lines would be

consistent with the presence of a small amount of  $\alpha$ -calcium orthophosphate in the irradiated enamel. According to that investigation, the presence of  $\alpha$ -calcium orthophosphate in the irradiated enamel was also indicative of a high transient temperature at the irradiation site. Furthermore it has been stated (Vahl, 1968, 1971) that the X-ray diffraction analysis of the lased enamel substance, caught from the laser plume, indicated that it was tricalcium phosphate, not hydroxyapatite. The powder sample used in these diffraction photographs was derived from the enamel substance being vaporized by laser irradiation. To our knowledge the studies mentioned above are the only published ones in which crystallographic methods have been used to clarify the character of the structural

---

Received for publication, June 20, 1973.

changes induced by laser effects in the apatite structure of dental hard tissues. These changes do in fact occur, and they are easily perceptible by means of both polarized light microscopy and X-ray microanalysis (Kantola, 1972a,b).

The aim of the present study was to elucidate, with the aid of X-ray diffraction, the crystallographic nature of the changes induced by laser-effects in dental enamel and to corroborate the results obtained in the studies mentioned above.

#### MATERIALS AND METHODS

The tooth material in this study consisted of intact teeth extracted for orthodontic reasons. The teeth crowns were subjected to irradiation produced by the laser-beam of CO<sub>2</sub> laser (Siemens, Munich), the output power of which was 100 W.

This produced a distinct effect in the enamel resembling that of burning. This effect was produced with irradiation of the enamel for about 2—3 seconds, the energy density being approximately 10<sup>4</sup>—10<sup>5</sup> J/cm<sup>2</sup>. Enamel powder for the X-ray diffraction study was made both from intact enamel and from enamel particles distinctly subjected to laser-irradiation, by means of grinding, partly with a diamond disc and partly in an agate mortar. The 0.5 mm glass capillaries used in Debye-Scherrer photography were filled with the powder samples. The diffraction patterns of the powder samples were obtained with a camera of 114.6 mm diameter using CuK $\alpha$  radiation. The films were exposed at 32 kV and 16 mA for 28 hours.

The  $2\theta$ -values of the diffraction lines were measured with a simple nonius goniometer. The photometer curves were also taken for the films in order to check

the positions of the diffraction lines at low  $2\theta$  angles.

For the sake of comparison, Debye-Scherrer diffraction photographs were also taken of a sample of natural hydroxyapatite.

The diffraction intensity curves for the powder samples in question were taken with a Siemens Kristalloflex IV diffractometer. A Si(Li) semiconductor detector and pulse height analyser were employed in this study in determining intensity, instead of the normal scintillation detector with photomultiplier and amplifier. In this way high peak/background ratios and better resolution can be obtained than with other detectors (Laine & al., 1972). In the diffractometer analysis CuK $\alpha$  radiation was also employed.

#### RESULTS

Several Debye-Scherrer photographs were taken of the powder samples obtained from untreated normal enamel and from laser-treated enamel. The photograph of the diffraction film No. 3, of normal enamel, can be seen in Fig. 1a; the photograph of the diffraction film No. 6, of the laser-treated enamel, can be seen in Fig. 1b; and the photograph of the diffraction film No. 2, of powdered natural hydroxyapatite, in Fig. 1c.

When the diffractographs of natural hydroxyapatite with those of different enamel samples are compared, it can be said, judging by the eye, that they quite obviously represent diffractographs of the same substance; the positions of the diffraction lines and the intensity ratios are clearly identical in all these cases. A further examination of the diffractographs reveals that the lines of diffractographs obtained from natural hydroxyapatite

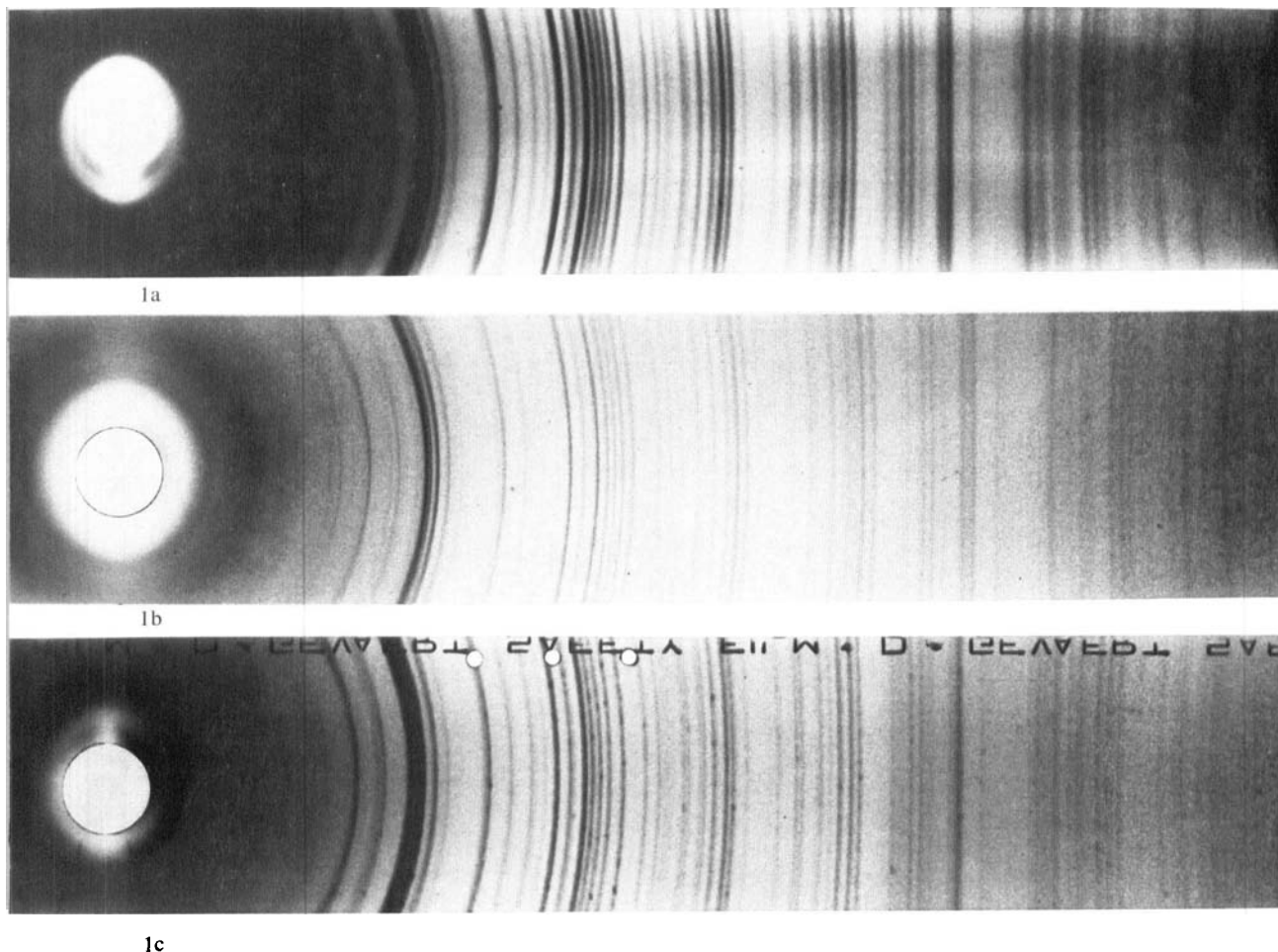


Fig. 1. a. Debye-Scherrer pattern from unlased enamel  
 b. Debye-Scherrer pattern from lased enamel  
 c. Debye-Scherrer pattern from natural hydroxyapatite

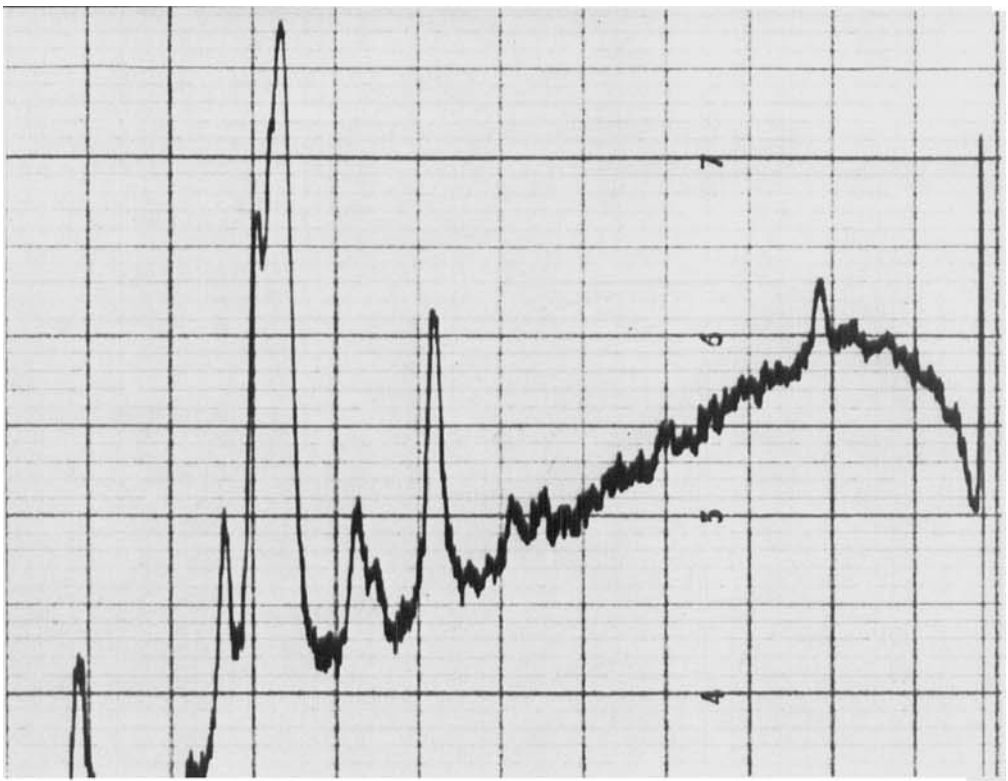
and lased enamel are clearly sharper than those of the diffractographs of normal enamel. It can be estimated on the basis of the width and shape of the diffraction lines that the size of the crystallites is greatest in the apatite sample,  $10^{-4}$ – $10^{-3}$  cm, whereas it is approximately  $10^{-5}$  cm in the lased enamel sample and even smaller by one order of magnitude in the normal enamel. The  $2\theta$  values of the diffraction lines measured from the films of Fig. 1 and their respective spacings,  $d$ , are shown in Table I. The spacings,  $d$ , have been

calculated according to Bragg's equation  $d = \frac{\lambda}{2 \sin \theta}$  using the value of  $1.54178 \text{ \AA}$  for the wavelength of  $\text{CuK}\alpha$  radiation. The calculations were carried out on an UNIVAC 1108 digital computer using a special program which also provided for shrinking in the process of developing the films. In addition, in Table I there are the spacings  $d$  for hydroxyapatite given in the ASTM standard table 9-432, their Miller-indices (hkl) and the intensity ratios  $I/I_1$  in comparison with the intensity of

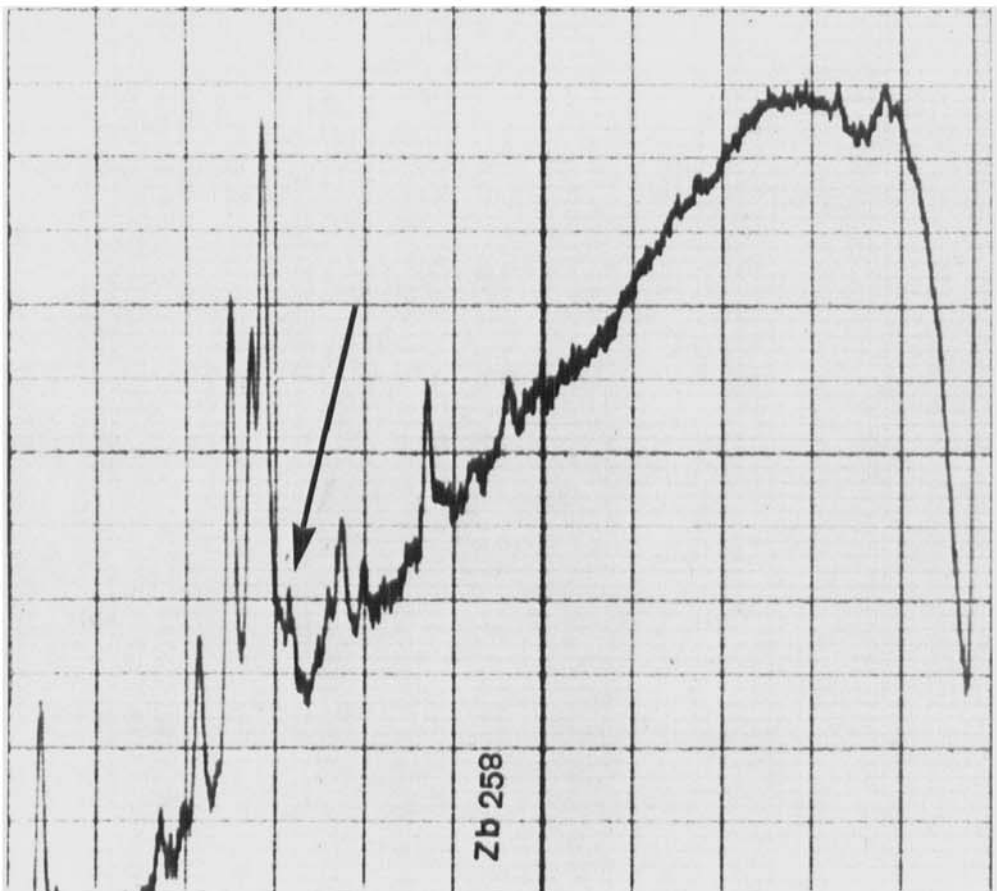
Table 1. Comparison of spacings obtained from film measurements with ASTM-spacings

Hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ASTM-card 9-432			Debye-Scherrer film						$\alpha\text{-Ca}_3(\text{PO}_4)_2$ ASTM-card 9-348				$\beta\text{-Ca}_3(\text{PO}_4)_2$ ASTM-card 9-169				
Apatite Film 2		Enamel Film 3		Lased enamel Film 6						$\alpha\text{-Ca}_3(\text{PO}_4)_2$		$\beta\text{-Ca}_3(\text{PO}_4)_2$					
hkl	$1/I_1$	d Å	$2\theta^{**}$ calc	$2\theta^{\circ}$ obs	$d^{**}$ calc	$2\theta^{\circ}$ obs	$d^{**}$ calc	$2\theta^{\circ}$ obs	$d^{**}$ calc	hkl	$1/I_1$	d Å	$2\theta^{**}$ calc	hkl	$1/I_1$	d Å	$2\theta^{**}$ calc
100	12	8.17	10.83	10.8	8.17	10.5	8.42							012	12	8.15	10.86
										111	25	7.31	12.11	104	16	6.47	13.69
										130	10	6.29	14.08	110	20	5.21	17.02
										201	10	5.83	15.20				
										1311 040}	12	5.18	17.12				
200	10	4.07	21.84			21.6	4.11	22.1	4.02					024	16	4.06	21.89
										150	20	4.00	22.22				
										202	40	3.91	22.74				
111	10	3.88	22.92	22.8	3.89	22.9	3.88	23.1	3.85	241	40	3.88	22.92				
										132	40	3.69	24.12				
										1511 222}	18	3.66	24.32				
002	40	3.44	25.90	25.9	3.43	25.8	3.45	26.1	3.41					1.0.10	25	3.45	25.82
										510	20	3.01	29.68				
102	12	3.17	28.15			28.0	3.19	28.4	3.14	113	20	2.947	30.33	122	10	3.36	26.52
210	18	3.08	28.99	28.7	3.10	28.8	3.10	29.3	3.05	402	35	2.919	30.63	214	55	3.21	27.79
										441 170}	100	2.905	30.78	300	16	3.01	29.68
														217 0.2.10}	100	2.880	31.05
211	100	2.814	31.80	31.7	2.816	31.6	2.831	32.0	2.797	511	30	2.860	31.27				
										530	12	2.786	32.13				
112	60	2.778	32.22	32.3	2.765	32.8	2.730	32.4	2.763					128	20	2.757	32.47





2a



2b

Fig. 2. a. Photometric curve from Debye-Scherrer film of unlased enamel (Fig. 1a)  
 b. Photometric curve from Debye-Scherrer film of lased enamel (Fig. 1b)

the strongest line. Furthermore, in order to facilitate the comparison, the  $2\theta$  values corresponding to the standard spacing for  $\text{CuK}\alpha$  radiation have been calculated.

In addition, the respective corresponding values for  $\alpha$ -calcium orthophosphate given in the ASTM-standard table 9—348 and for  $\beta$ -calcium orthophosphate given in the ASTM-standard table 9—169 have been listed in Table I. It can be seen that within the accuracy of measurement the spacings obtained from the Debye-Scherrer films correspond with the spacing values of hydroxyapatite given in the ASTM-Powder Diffraction Data File.

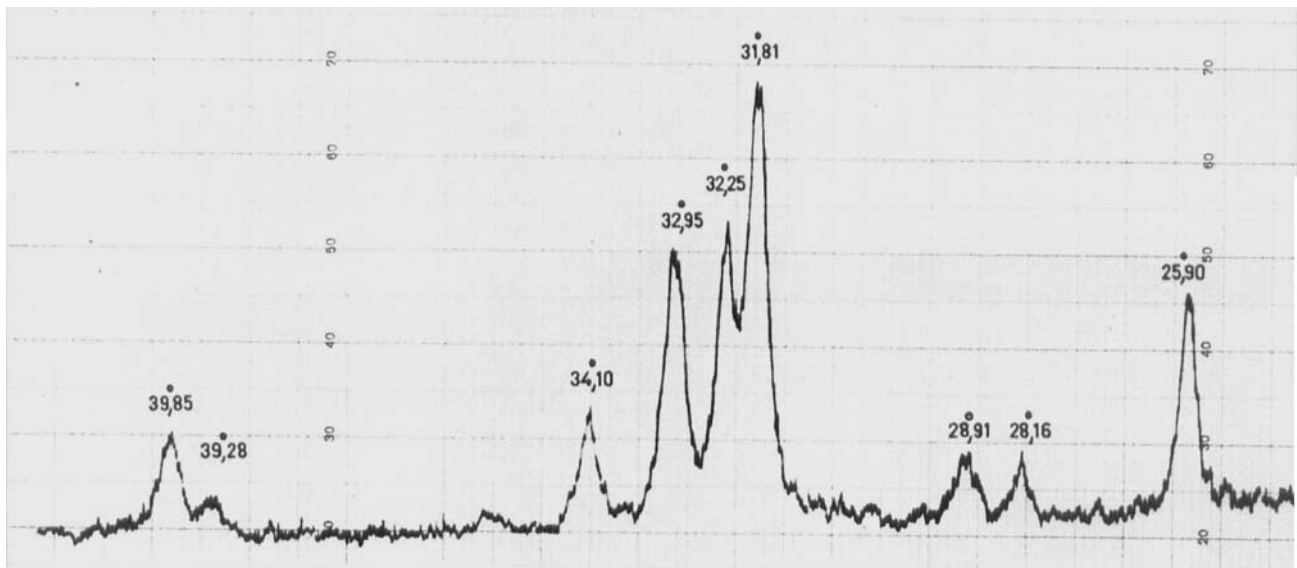
As control material, photometergraphs were taken of films No. 3 and 6, that is the low angle side of the Debye-Scherrer patterns of normal and lased enamel. They are shown in Figures 2a and 2b. When photometering, the speed of the recording paper was 3.1 x the speed of the film. Consequently, the  $2\theta$  values of the lines of the film can be calculated from the positions of the peaks in the recording paper. All the lines measured from the films are distinctly visible in the photometric curves. The  $2\theta$  values determined from the photometric curves are, within the accuracy of measurement, exactly identical with the  $2\theta$  values obtained from the film measurement. In the photometric curve of film No. 6 (Fig. 2b), that is the photometric curve of the Debye-Scherrer photograph of lased enamel, there is a weak, but distinct maximum,  $2\theta=30^\circ.8$ , (arrow) beside the strongest line,  $2\theta=31^\circ.9$ .

It was not observed with the aid of the nonius gradometer when reading the film. This peak, corresponding with the spacing-value  $2.90 \text{ \AA}$ , does not exist in the photometric curve of the powder pattern of normal enamel. The only other difference in the photometergraphs of the diffrac-

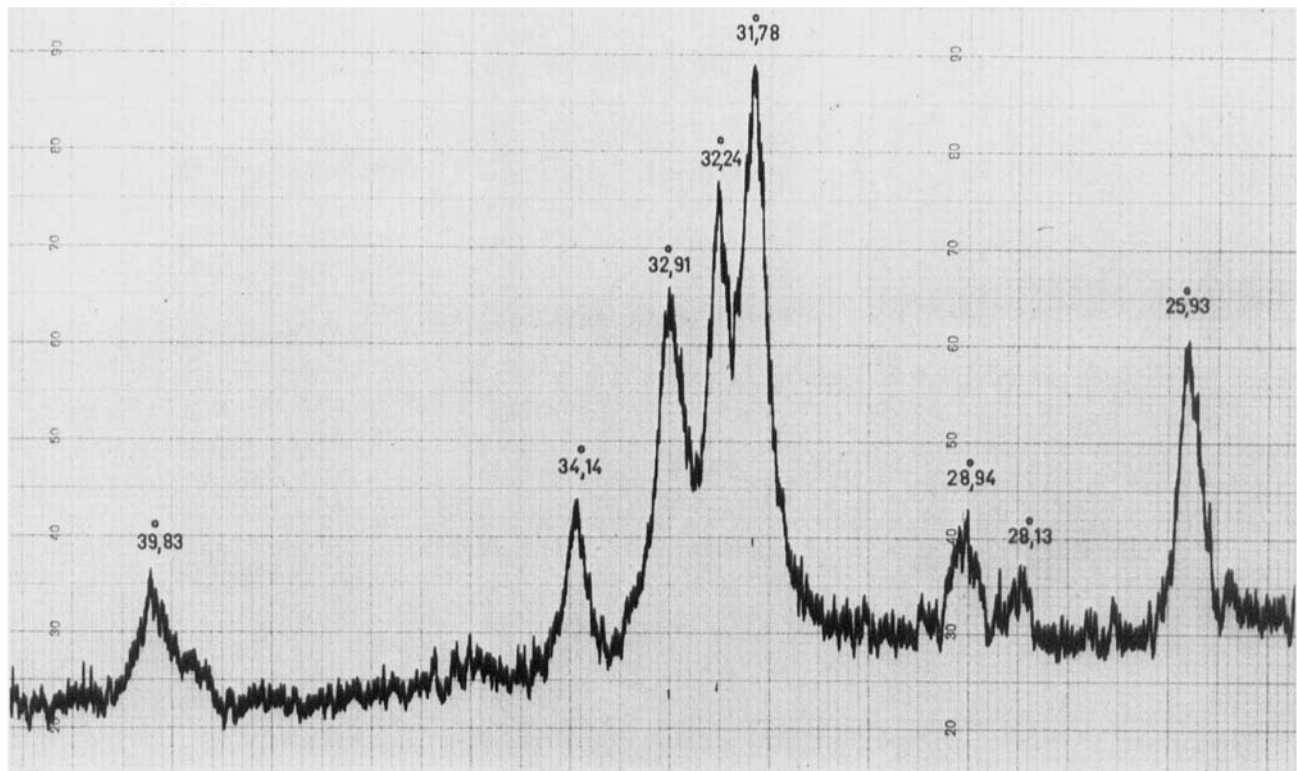
tion patterns obtained for normal and lased enamel is the fact that the intensity peaks in the photographs of lased enamel are distinctly narrower, in other words sharper, than those of normal enamel, a fact that could already be observed earlier on the basis of a gross estimate of the films.

It can be seen in the photometric curves how background blackening, especially in case of the lines at low  $2\theta$  values, hinders the observation of weak lines. For this reason and in order to obtain a control, the intensity curves of the said samples were also taken with the aid of a diffractometer. Figures 3a, 3b and 3c illustrate the diffractometric intensity curves of apatite, normal enamel and lased enamel, obtained primarily from the angle-region  $22^\circ < 2\theta < 40^\circ$ . As control material the intensity curve of lased enamel was taken down to as low an angle as possible within the capacity of the diffractometer used, that is  $2\theta=12^\circ$ . In the Figures mentioned above the corresponding  $2\theta$  values have been marked beside the peaks. The systematic deviation due to the small alterations in the position of the sample has been rectified so that by comparing the observed  $2\theta$  values of the lines (002) and (211) with their respective ASTM-values, a small error, of at most two or three tenths of a mm, in the position of the sample could be calculated (Parrish, 1965) and its influence accounted for the  $2\theta$  values of the peaks.

It can be observed that the positions and the intensities of the peaks of the intensity curves obtained from different samples are nearly in complete agreement with each other. Only in the case of the diffractometric intensity curve obtained for lased enamel (Fig. 3c), is a small peak in the position  $2\theta=30^\circ.81$  perceptible, which is absent from the other curves.

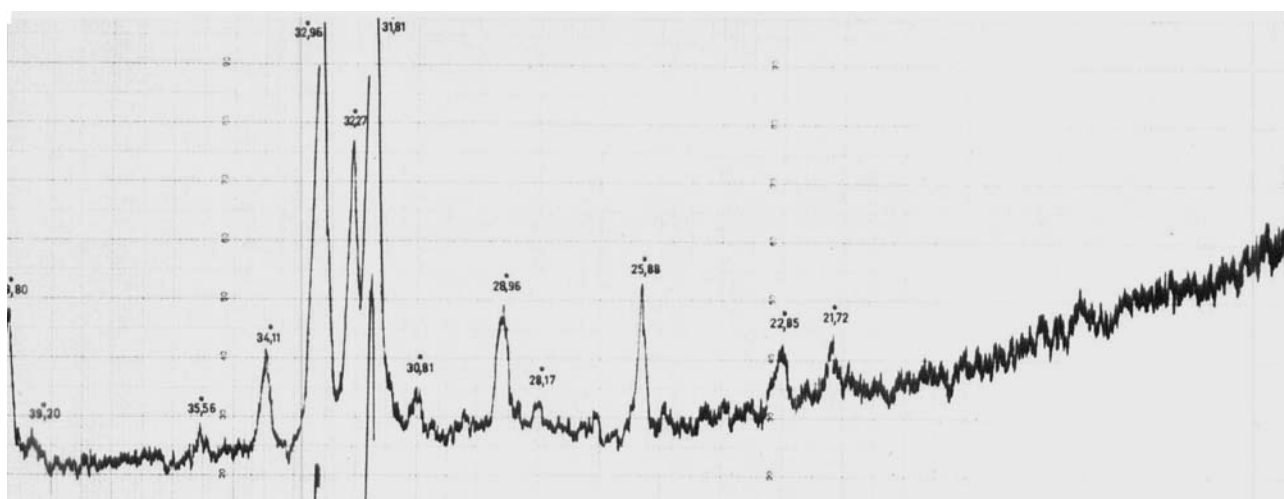


3a



3b

Fig. 3. Diffractometric intensity curves obtained with a diffractometer using a Si(Li) semiconductor detector and pulse height analyser  
 a. Diffractometric curve from apatite  
 b. Diffractometric curve from unlased enamel  
 c. Diffractometric curve from lased enamel



3c

The spacing values of hydroxyapatite, alpha calcium orthophosphate and beta calcium orthophosphate given in the ASTM-standard tables (9—432, 9—348 and 9—169) corresponding with the peaks of the diffractometric curves in the region  $22^\circ < 2\theta < 40^\circ$  are presented in Table II. Their respective Miller-indices and the intensity ratios in comparison with the strongest line are also shown in Table II. It can be noted that the peak  $2\theta = 30^\circ.81$  obtained for lased enamel, corresponding with the spacing  $d = 2.902 \text{ \AA}$ , fits almost exactly the strongest line of alpha calcium orthophosphate (441, 170) when  $d = 2.905 \text{ \AA}$ . This indicates that a small amount of alpha calcium orthophosphate,  $\alpha\text{-Ca}_3(\text{PO}_4)_2$  exists in the lased enamel.

#### DISCUSSION

Powerful  $\text{CO}_2$  laser irradiation produces phenomena of fusing and recrystallization in enamel observable even by means of macroscopic studies. By comparing the X-ray diffraction patterns of hydroxyapatite obtained from the powder samples of normal and lased enamel, recrystallization and growth in crystallite

size connected with it due to laser-induced effects can be observed. In the diffractograph of the lased sample there can also be seen a weak but distinct maximum, with the spacing value of  $2.902 \text{ \AA}$ , which almost exactly fits the strongest line of alpha calcium orthophosphate (441, 170), but which is absent from the diffractograph of hydroxyapatite. According to this result, some amount of the high-temperature form of the apatite phase of tricalcium phosphate, has been formed due to the laser-effect and still exists at room temperature (*Gmelins Handbuch, Van Wazer, 1958*). The same conclusion was drawn in the study mentioned in the introduction (*Lobene et al., 1968*). However, the strongest diffraction line of alpha calcium orthophosphate now substantiated was not observed in the latter study; instead, there were only weak lines perceptible, the intensities of which were, according to the ASTM-standard table, 0.25, 0.10 and 0.40 of the intensity of the strongest line. According to *Gmelins Handbuch*, alpha calcium orthophosphate is positively birefringent in its optical properties. In a previous study (*Kantola, 1972b*), a layer (IV) could be seen in the



