

Experimental study of the system fluorapatite-chlorapatite under 10 and 12 kbar at 640, 750 and 900°C

(fluorapatite/chlorapatite/solid solution)

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ABSTRACT Fluorapatite (FA), chlorapatite (CA), and five intermediate members (FA₉₀CA₁₀, FA₇₀CA₃₀, FA₅₀CA₅₀, FA₃₀CA₇₀ and FA₁₀CA₉₀) were synthesized by mixing appropriate chemicals. The mixtures were subjected to following P-T conditions: 8 kb-640°C, 10 kb-750°C and 12 kb- 900°C. A complete solid solution between two end members could be established from refractive index and cell parameter measurements. A plot of the F-Cl contents vs. composition of the starting materials show a gradual decrease in F with increase in Cl content and a negative slope. A careful study of apatites from nature should reveal a continuous spectrum from F-rich to Cl-rich apatite.

Apatite, a commonly occurring phosphate is found as an accessory mineral in silica-undersaturated peridotites and feldspathoidal rocks through intermediate rock series to silica-saturated varieties, belonging to granitoid family. Thus, in the normative analysis of a rock, P₂O₅ is generally assigned to apatite.

There are four main varieties of apatite¹: Fluorapatite [Ca₅(PO₄)₃ F], Chlorapatite [Ca₅(PO₄)₃ Cl], Hydroxylapatite [Ca₅(PO₄)₃ OH] and Carbonate-apatite [Ca₅(PO₄)₃ CO₃ OH]₃(F,OH)]. Among all these, fluorapatite is by far the most common one, followed by hydroxylapatite. Extensive substitution of F and Cl is very common in case of fluorapatite.

Preliminary experimental studies² on the system CaF₂-Ca₃(PO₄)₂ show that it is

binary with an eutectic at [(CaF₂)₆₀ {Ca₃(PO₄)₄₀}]. This system is quite different from that of the system² CaCl₂ - Ca₃(PO₄)₂, where there is also an eutectic at [(CaCl₂)₉₅ {Ca(PO₄)₅}]. Detailed studies have not been performed afterwards. Liquidus phase boundaries in the system CaF₂ -Ca(OH)₂ -CaCO₃ -Ca₂(PO₄)₂ have already been established³. Study of the system CaO-P₂O₅ -CaF₂ established a continuous solid-solution in the system (Ca₁₀(PO₄)₆F₂ and Ca₇(PO₄)₄F₂) but the system chlorapatite-fluorapatite has not been studied.

Since F and Cl are the members of the same group (Group VII-B) of the periodic table and have comparable ionic radii (1.35 Å and 1.81 Å respectively), it was thought that extensive substitution between F and Cl in apatite structure may be possible to give a continuous variation.

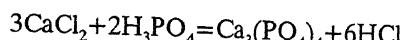
Following P-T conditions have been arbitrarily chosen to study the aforesaid system: 8 kb and 640°C, 10 kb and 750°C and 12 kb and 900°C. Temperatures for the experimental runs were chosen assuming a geothermal gradient of 25°C/km. These P-T conditions correspond to that of lower crustal region and crust-mantle boundary beneath the stable continental cratonic areas. Investigation related to variations in

cell-parameters, axial ratio, cell volumes was also part of the study. Attempt was also made to study the effect of P-T conditions and compositions pertaining to variation in the refractive indices.

Preparation of starting material : Reagent grade calcium chloride (CaCl_2), calcium fluoride (CaF_2) and orthophosphoric acid (H_3PO_4) were used as a source of chlorine, fluorine and phosphate, respectively to prepare chlorapatite and fluorapatite.

Calcium orthophosphate ($\text{Ca}_3(\text{PO}_4)_2$) was prepared by the following techniques: Calcium chloride was at first crushed to fine powder in an agate mortar, then it was heated in an oven at 60°C for 24 hours to get rid of moisture. Confirmation of calcium chloride was made from X-ray diffraction pattern. Taking CaCl_2 in a beaker, concentrated H_3PO_4 was added to it, then distilled water was poured in it and stirred well with the help of a glass rod. Exothermic reaction took place during the mixing of CaCl_2 and H_3PO_4 resulting in a white precipitate. The solution was kept for 24 hours, and then filtered. The filtrate was thoroughly washed with distilled water and then dried in an oven. X-ray diffraction pattern was taken to confirm the synthesis of apatite.

Calcium hydrogen phosphate (CaHPO_4) was also heated for 48 hours at 800°C to prepare $\text{Ca}_3(\text{PO}_4)_2$, but this method was not found to be suitable. It was observed that mixing of concentrated H_3PO_4 and CaCl_2 in a beaker in appropriate proportion resulted in the precipitation of $\text{Ca}_3(\text{PO}_4)_2$. The relevant reaction is as follows:



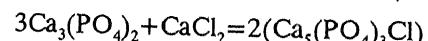
The residue was transferred in a

platinum crucible and heated in a silicon carbide furnace at 950°C for 48 hours, and a solid white cake was obtained, which was subsequently crushed to fine powder. The powder was heated again at 1450°C , in a molybdenum disilicide furnace for 4 hours. Crushing and heating operation was repeated twice. The X-ray pattern of the yield, confirmed that it was $\beta\text{-Ca}_3(\text{PO}_4)_2$.

Preparation of fluorapatite and chlorapatite : Fluorapatite was prepared by mixing $\text{Ca}_3(\text{PO}_4)_2$ with CaF_2 . Note the reaction : $3\text{Ca}_3(\text{PO}_4)_2 + \text{CaF}_2 = 2(\text{Ca}_5(\text{PO}_4)_3\text{F})$

CaF_2 was first confirmed by X-ray pattern. Then CaF_2 was added stoichiometrically with required amount of beta- $\text{Ca}_3(\text{PO}_4)_2$. They were mixed thoroughly in an agate mortar using acetone to homogenize the mixture. The powdered mixture was transferred into a platinum crucible and heated in a silicon carbide furnace twice at 700°C for 24 hours. A blue cake was formed which was crushed to fine powder. Formation of fluorapatite was confirmed by X-ray pattern.

Chlorapatite was also prepared by mixing appropriate proportion of calcium phosphate and calcium chloride in a platinum crucible. The mixture was stirred with a kanthal wire. Note the reaction,



The mixture was heated in a kanthal wire-wound resistance furnace. Acetone was not used in this mixing process and the platinum crucible was heated at 700°C for 48 hours. This heating was accompanied by subsequent crushing and once more heating. A white coloured solid cake was formed, which was crushed to fine powder, and formation of chlorapatite was confirmed by X-ray pattern.

Table 1-

Run no.	Composition	Temp. (°C)	Pressure (Kb)	Dura- tion (min.)	c (A)	a (A)	c/a
1.	FA ₇₀ CA ₃₀	640	8	120	6.878	9.373	0.734
2.	FA ₃₀ CA ₇₀	"	"	"	6.747	9.630	0.701
3.	FA ₉₀ CA ₁₀	"	"	"	6.8243	9.4179	0.7246
4.	FA ₁₀ CA ₉₀	"	"	"	6.6310	9.6808	0.6850
5.	FA ₇₀ CA ₃₀	750	10	205	6.9002	9.3957	0.7344
6.	FA ₃₀ CA ₇₀	"	"	"	6.8724	9.4224	0.7294
7.	FA ₉₀ CA ₁₀	"	"	55	6.8854	9.3856	0.7336
8.	FA ₁₀ CA ₉₀	"	"	"	6.8584	9.4982	0.7221
9.	FA ₇₀ CA ₃₀	900	12	60	6.9008	9.4025	0.73339
10.	FA ₃₀ CA ₇₀	"	"	"	6.668	9.527	0.701
11.	FA ₉₀ CA ₁₀	"	"	120	6.8992	9.3908	0.7347
12.	FA ₁₀ CA ₉₀	"	12	120	6.7105	9.5963	0.7183
13.	FA ₁₀ CA ₉₀	640	8	185	6.826	9.478	0.72

Table 1 contd.

Run no.	Cell Vol. (A ³)	d-values		Refractive indices	
		hkl (221) (A)	hkl (300) (A)	Temp. Correction = 0.000455/°C	
		omega	Eita		
1.	261.648	2.8177	2.7056	—	—
2.	270.92	2.8143	2.7203	—	—
3.	262.101	2.8106	2.7187	—	—
4.	269.093	2.7967	2.7527	—	—
5.	263.7671	2.8076	2.7123	—	—
6.	264.1996	2.8148	2.720	—	—
7.	262.6358	2.8068	2.7094	—	—
8.	267.918	2.8249	2.7573	—	—
9.	263.17	2.8147	2.7143	1.6363	1.6303
10.	266.82	2.8248	2.7510	1.6403	1.6303
11.	263.454	2.8071	2.7109	1.6343	1.6278
12.	267.586	2.8404	2.7702	1.6503	1.6403
13.	265.522	2.823	2.736	—	—

Table 2 -Standard data for fluorapatite and chlorapatite

	Fluorapatite	Chlorapatite
Mol. wt.	504.313	520.767
F%	3.768	0
Cl%	0	6.808
<i>c</i> (A)	6.87	6.76
<i>a</i> (A)	9.35	9.61
<i>c/a</i>	0.7348	0.7040
Cell Volume (A) ³	261.70	272.75
<i>d</i> -values (A) (211)	2.800	2.850
<i>d</i> -values (A) (300)	2.702	2.707
R.I. (eita)	1.629	1.667
omega	1.634	1.644

After preparing the two end members, fluorapatite and chlorapatite, the intermediate members were prepared by mixing the two end members in appropriate proportions. Four intermediate compositions were prepared $FA_{90}Ca_{10}$, $FA_{70}Ca_{30}$, $FA_{30}Ca_{70}$ and $FA_{10}Ca_{90}$ with the weight ratio of fluorapatite : chlorapatite equal to 9:1, 7:3, 3:7 and 1:9. The mixing was done with the help of acetone in an agate morter. Repeated addition of acetone, mixing and drying was necessary to homogenize the mixture. Thus, the starting materials were ready for experiments.

Apatite was identified with the help of a transmitted light optical microscope. The refractive indices of the run products were measured with the help of refractive index liquids, supplied by Cargill Laboratory, U.S.A. The results are given in Table 1.

Powdered sample was studied with the help of a X-ray diffractometer (Seifert: XRD 3000 P). Only apatite was present in all the run products.

Thirteen runs have been performed in the high-pressure piston-cylinder apparatus with four intermediate compositions $FA_{90}CA_{10}$, $FA_{70}CA_{30}$, $FA_{30}CA_{70}$ and $FA_{10}CA_{90}$. Experiments have been made under pres-

sures 8, 10 and 12 kb and temperatures 640°, 750° and 900°C, respectively. Runs of longer durations were needed for the lower *P-T* conditions to reach perfect equilibrium.

Unit cell parameters (*a* = 9.37, *c* = 6.88 for fluorapatite and *a* = 9.63, *c* = 6.78 for chlorapatite) are already available⁵. The *d*-values of two main reflections (211 and 3000) for the two end members have been chosen from the values given in ASTM cards. In case of run products at a given pressure and temperature, variations in the intermediate compositions were observed.

Plots of *d*-values for 211 and 300 reflections (Fig. 1 & 2) at 640° (8 kb), 750° (10 kb) and 900°C (12 kb) show continuous increase in *d*-values from fluorapatite to chlorapatite. The values of *a* (Fig. 3) show continuous increase; whereas those of *c* (Fig. 4) indicate gradual decrease with increase in chlorapatite content. These values agree with those of the two end members. It is evident from the above results that with the increase in Cl- content, the apatite crystals change their shape from elongated prismatic to tabular one. Axial ratio (*c/a*) plot (Fig. 5) shows only slight variation with continuous decrease in Cl-content. The effect of decrease in the values of *c* is thus, more pronounced with respect to that of *a* resulting in the decrease in the axial ratio. Cell volume increases gradually (Fig. 6) from fluorapatite end to chlorapatite. This may be due to higher electronegativity of F than Cl, thereby causing a decrease in the volume of F-rich apatites with respect to that of Cl-rich one. Since pressure and temperature both were variable, it was not possible to draw any isothermal section and study correlation pattern of cell volume for crystals formed at different *P-T* conditions.

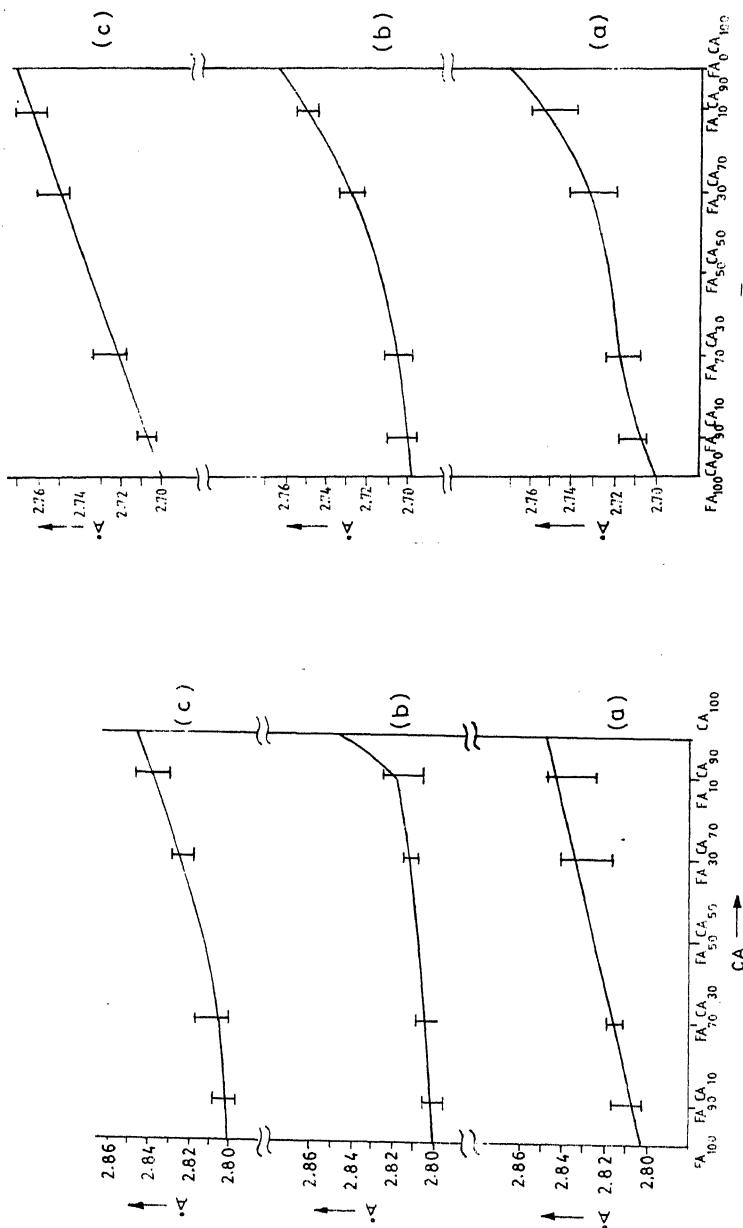


Fig. 1 - Variation of d -value of reflection (211) of fluorapatite-chlorapatite with respect to composition.

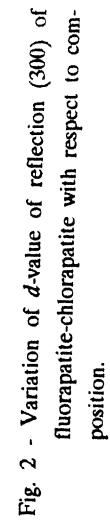


Fig. 2 - Variation of d -value of reflection (300) of fluorapatite-chlorapatite with respect to composition.

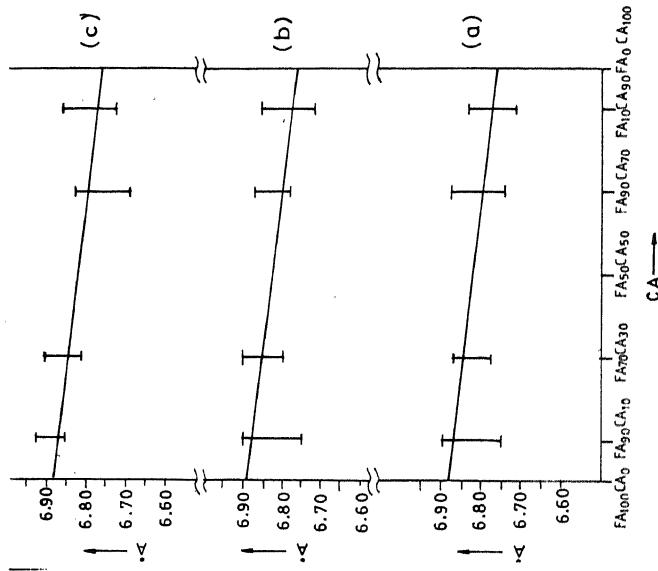


Fig. 4 - Plot of c with respect to composition.

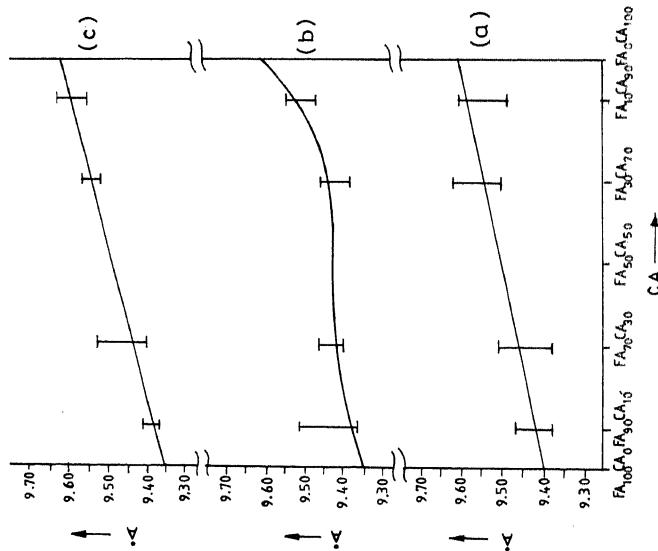


Fig. 3 - Plot of α with respect to composition.

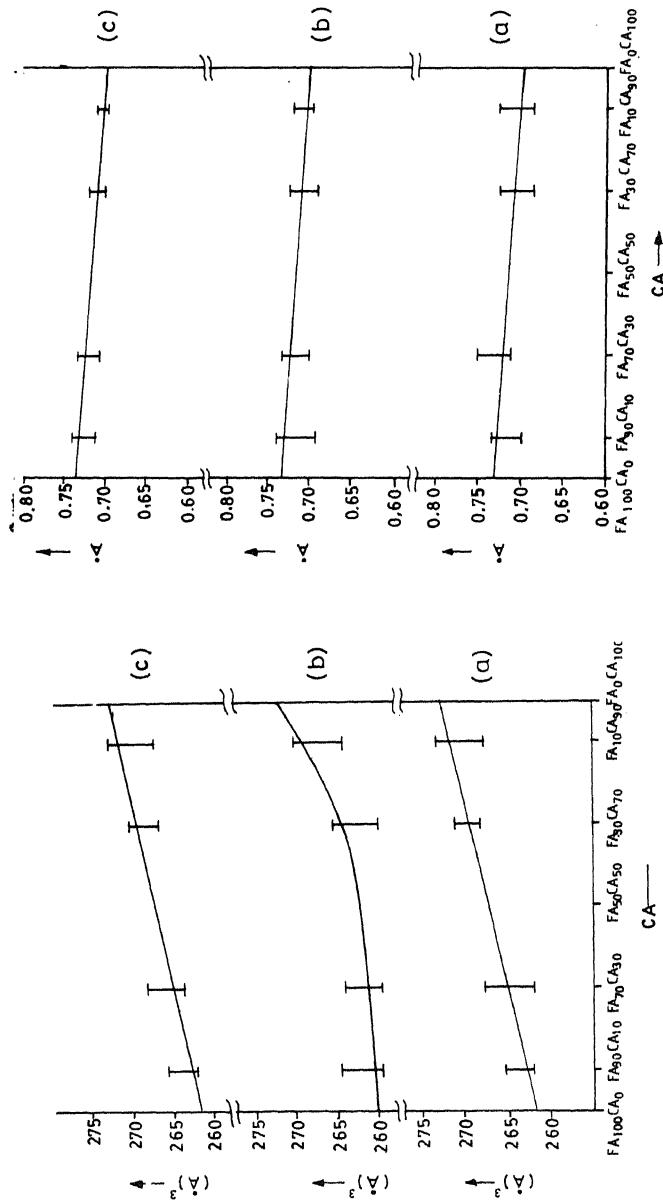


Fig. 5 - Plot of axial ratio (c/a) with respect to composition.

Fig. 6 - Plot of cell volume with respect to composition.

Refractive indices (both ϵ and ω) of the run-products were measured by Becke-line method. Plot of refractive indices values (Fig. 7 & 8) with respect to composition, show that variation in these properties are also continuous as expected from the measurement of the cell edges. The uncertainty limits are denoted by the vertical bars in Figs. (1-6).

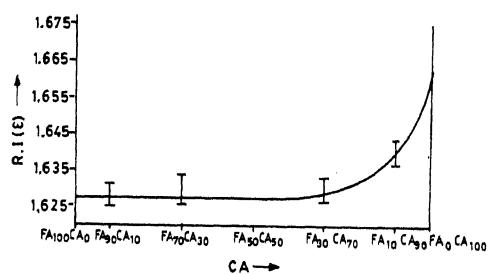


Fig. 7 - Variation in the refractive index value (ϵ) with respect to composition.

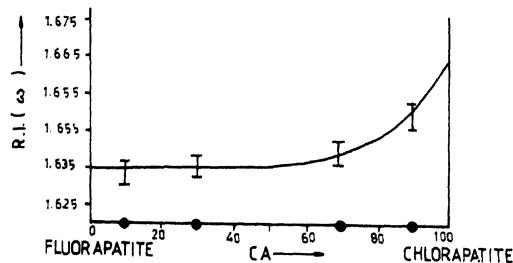


Fig. 8 - Variation in the refractive index value (ω) with respect to composition.

Figs. (1-8) confirm that there is a continuous variation in the physical, optical and crystallographic properties from one end to other. No sharp discontinuity in the data have been noted. Thus, it can be concluded that continuous solid solutions occur between fluor and chlorapatite under pressure-temperature conditions existing in the lower crust and in the crust-mantle boundary.

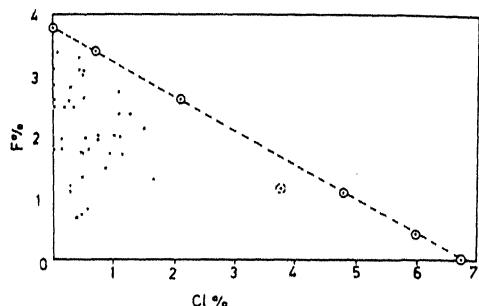


Fig. 9 - Plot of Cl and F-content of natural apatites with respect to their synthetic equivalents.

Microprobe analyses of F and Cl content of apatites from quartz- monzonites, granodiorites and diorites are available⁶. Plot of these values (Fig. 9) show a cluster around F-rich end ($FA_{90}CA_{10}$ and $FA_{70}CA_{30}$). These values are slightly lower than the ideal ones, which is possibly due to the presence of hydroxyl ion, not considered in the present study. Lack of microprobe facilities inhibit the estimation of Cl and F entering into the structure of apatite under the chosen P-T conditions. A plot of the F-Cl contents of the starting materials (Fig. 2) shows a negative slope with gradual decrease in F with the increase in Cl content. Similar negative trend has been observed by various workers⁶⁻⁹. All the data show a cluster around F-rich end. But the analyses of one apatite by Harada¹ shows that Cl-rich apatite is also available in nature. Thus, it proves that extensive solid-solution occurs between fluor and chlorapatite although Cl content is restricted to a certain limit in presence of hydroxyl ions.

REFERENCES

1. Deer, W.A., Howie, R.A. & Zussman, J. (1962) *Minerals* 5 : 323.

- 2. Nacken R. (1912) *Zentr. Mineral. Geol.* 550.
- 3. Wyllie, P. J. (1967) *J. Am. Ceram. Soc.* 50 (1) : 45.
- 4. Berak, J. & Tomczak-Hudya. T. (1972) *Roczn. Chem.* 46 (12) : 2157.
- 5. McConnell, E. (1973) *Apatite, its crystal chemistry, mineralogy, utilization and geologic and biologic occurrences*, Springer Verlag, III p.
- 6. Roegge, J.S., Logsdon, M.J., Young, H.S., Barr, H.B., Borcsik, M. & Holland, H.D. (1974) *Econ. Geol.* 69 : 229.
- 7. Nash, W.P. (1972) *Am. Mineral.* 57 : 877.
- 8. Toborszky, F. K. (1962) *Beitr. Zur Mineralogie Petragraphie* 8 : 354.
- 9. Stormer, J.C. & Carmichael, I.S.E. (1971) *Contr. Mineral and petrol.* 31 : 121.