

12 June 1985; Revised 20 May 1986

1. Ramamoorthy, S. and Manning, P. G., *Inorg. Nucl. Chem. Lett.*, 1974, **10**, 109.
2. Misra, A., Mittal, S. and Chaturvedi, G. K., *J. Indian Chem. Soc.*, 1980, **57**, 42.
3. Kapoor, K., Vinod Kumari, Sharma, R. C. and Chaturvedi, G. K., *J. Indian Chem. Soc.*, 1977, **54**, 687.
4. Sujata Khanna, Rajiv Kumar and Chaturvedi, G. K., *Indian J. Chem.*, 1980, **A19**, 766.
5. Gladefetter, W. L. and Gray Harry, B., *J. Am. Chem. Soc.*, 1980, **102**, 555.
6. Biswas, S. P., Krishnamoorthy, T. S. and Venkateshwarshi, C., *Indian J. Chem.*, 1980, **A19**, 710.
7. Biswas, S. P., Krishnamoorthy, T. S. and Venkateshwarshi, C., *Indian J. Chem.*, 1978, **A16**, 972.
8. Vogel, A. I., *A textbook of quantitative inorganic analysis*, 1962, Longman, London.
9. Chaberck, S. Jr. and Martell, A. E., *J. Am. Chem. Soc.*, 1952, **74**, 5052.
10. Anita Gupta, *Quaternary and binuclear ternary mixed ligand complexes of some transition metals*, Ph.D. thesis, Agra University, Agra, 1985.
11. Carey, G. H. and Martell, A. E., *J. Am. Chem. Soc.*, 1967, **89**, 3859.
12. Irving, H. and Williams, R. J. P., *J. Chem. Soc.*, 1953, **3**, 3192.

Ca-RICH PYROXENES FROM THE CARBONATITE COMPLEX OF TIRUPPATTUR, TAMIL NADU

R. RAMASAMY

Directorate of Geology and Mining, Madras 600 032, India.

IN order to study the change of composition of clinopyroxenes (cpx) during the course of magmatic differentiation, seven microprobe analyses of cpx from a series of alkaline rocks of the carbonatite complex of Tiruppattur¹ (N 12°15'–12°30' and E 78°25'–78°35') were carried out by using JXA 90 A (15 kV), computer-attached electron probe micro-analyzer, in the geochemical laboratory of Moscow State University, USSR. The chemical analyses (table 1) show that the cpx are calcium-rich and

straddle the $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFeSi}_2\text{O}_6$ join. By using the bulk rock analyses of associated alkaline rocks, compositions of a few cpx were also determined by the method of Rittmann² and were plotted along with the compositions of cpx obtained by microprobe analyses. All cpx are distinctly Ca-rich and fall near the field of Ca-rich cpx demarcated by Eriksson³, similar to cpx from Palabora carbonatite complex of Africa³. The diagram (figure 1) showing diopside-hedenbergite-acmite components of the analyzed cpx exhibits marked iron enrichment at late stages of magmatic fractionations. During the course of magmatic crystallization, increasing trend of Ca and Fe with decreasing trend Na and $\text{Mg}/(\text{Mg}+\text{Fe})$ was noted (table 1). Further, table 1 indicates that the cpx from the ultramafics show increase of Al with decrease in Si, while the syenites exhibit a decreasing trend of Al with increasing content of Si. DI of these cpx ($100 \text{ Mg}/\text{Mg}+\text{Fe}$) indicate two separate trends, one for ultramafics and another for syenites.

The carbonatite complex comprises a sequence of zoned co-magmatic members of alkali syenites, ultramafics and carbonatites in two adjacent independent structural basins designated as Sevvattur and Jogipatti basins. The host rocks of cpx indicate two separate trends of evolutions⁴:

1. Biotite-oligoclase → pyroxenite → biotite pyroxenite → apatite-magnetite-orthoclase-biotite pyroxenite

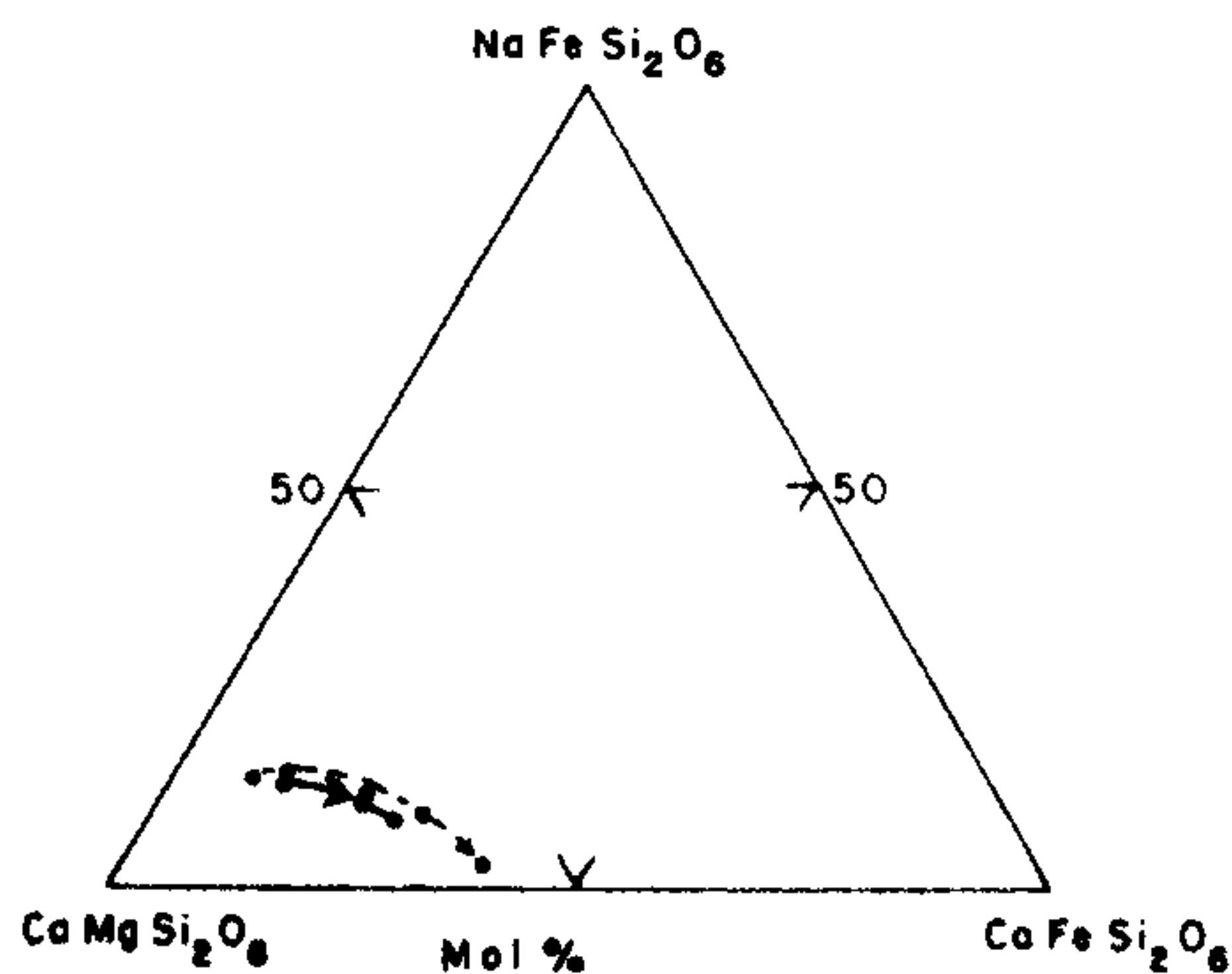


Figure 1. Crystallization trends of iron enrichment in calcium-rich pyroxenes from alkaline rocks of Tiruppattur (trend of pyroxenes from ultramafic rocks---; from syenites —).

Table 1 Microprobe analyses of clinopyroxenes from alkaline rocks of Tirupattur

	Ultramafics				Syenites			
	40	497	16	8	28	29	360	
SiO ₂	46.61	47.49	49.58	52.47	53.38	51.72	51.68	
Al ₂ O ₃	5.08	6.33	5.85	3.79	2.23	2.41	1.06	
FeO ^I	12.02	10.85	5.74	7.38	11.33	10.89	12.91	
MnO	11.16	0.19	0.20	0.30	0.62	0.61	0.22	
MgO	11.68	9.93	12.13	14.00	11.22	10.61	9.68	
CaO	22.21	22.19	22.51	19.69	20.64	21.61	21.78	
Na ₂ O	0.37	1.12	2.49	1.91	1.26	1.33	0.84	
TiO ₂	1.02	1.30	0.50	0.34	0.12	0.23	0.06	
Cr ₂ O ₃	0.10	0.01	0.02	0.01	0.05	0.07	-	
Total	99.25	99.41	99.02	99.89	100.85	99.48	98.23	
Numbers of ions on the basis of 6 (O)								
Si	1.797	2.00	1.863	2.00	1.939	2.00	1.988	
Al ^{IV}	0.203	0.185	0.137	0.061	0.061	0.012	0.012	
Al ^{VI}	0.028	0.100	0.120	0.103	0.087	0.072	0.087	
Ti	0.030	0.037	0.014	0.009	0.005	0.007	0.005	
Cr	0.003	-	-	-	0.002	0.003	0.002	
Mg	0.672	0.565	0.679	0.771	0.622	0.599	0.622	
Fe	0.387	0.347	0.181	0.229	0.354	0.347	0.347	
Mn	0.005	0.007	0.007	0.009	0.020	0.021	0.020	
Ca	0.917	0.910	0.905	0.780	0.824	0.878	0.824	
Na	0.028	0.082	0.180	0.138	0.090	0.096	0.090	
Mg	34.0	31.0	38.5	43.3	34.5	32.9	29.7	
Fe	19.6	19.1	10.2	12.9	19.7	19.0	22.3	
Ca	46.4	49.9	51.3	43.8	45.8	48.1	48.0	
(MgFe) ₂ SiO ₄	14.1	0.4	-	8.8	6.0	2.7	2.9	
Ca(MgFe)Si ₂ O ₆	85.9	99.6	96.0	83.9	87.0	92.7	93.0	
SiO ₂	-	-	4.0	7.3	7.0	4.6	4.1	
NaFeSi ₂ O ₆	2.9	9.0	13.1	12.7	9.9	10.9	7.8	
CaFeSi ₂ O ₆	38.0	29.0	7.9	11.4	21.3	20.6	25.2	
CaMgSi ₂ O ₆	59.1	62.0	79.0	75.9	68.8	68.5	67.0	
Ti+ Al ^{IV} /Si	0.13	0.12	0.08	0.04	0.01	0.02	0.001	
Ti/100 Mg(Mg+Fe)	0.47	0.60	0.18	0.12	0.08	0.11	0.050	
Al in Z	10.2%	9.3%	6.9%	3.1%	0.6%	1.9%	-	
Al ^{IV} /Al ^{VI}	7.25	1.85	1.14	0.59	0.14	0.51	0.02	
100 Mg/(Mg+Fe)	63.5	62.0	79.0	77.1	63.7	63.3	57.2	

FeO^I - FeO total; Analyst - Mr. V. K. Garamin; Pyroxenes from apatite-magnetite-orthoclase-biotite pyroxenite (40); Biotite pyroxenite (497); Biotite-oligoclase pyroxenite (16) Shonkinite (8); Augite syenite (28); Porphyritic augite syenite (29); Scapolite-melanite-aegirine augite-dioptside syenite (360).

2. Shonkinite → augite syenite/porphyritic augite syenite → scapolite-melanite-aegirine augite-diopside syenite

The ultramafic rocks of biotite-oligoclase pyroxenite and apatite-magnetite-orthoclase-biotite pyroxenite are the magmatic rocks found adjacent to older series of zoned carbonatites in the Sevattur basin and to younger series of zoned carbonatites in the Jogipatti basin respectively. The biotite-pyroxenite is a co-magmatic member found adjacent to apatite-magnetite-orthoclase-biotite pyroxenite. A melasyenite of shonkinite might have genetic link with the ultramafics and alkaline rocks. The late magmatic augite syenite appears to be a marginal variant of the porphyritic augite syenite which is emplaced at the centre of the Sevattur basin. The scapolite-melanite-aegirine augite-diopside syenite occurring in the centre of the Jogipatti basin along with carbonatites, appears to be the youngest syenitic member in this complex.

According to Wass⁵, low pressure cpx show higher ratios of $Ti/100 (Mg+Fe)$, Al^{iv}/Al^{vi} and $Ti+Al^{iv}/Si$. These parameters in the analyzed cpx (table 1) show that, cpx from ultramafics were crystallized towards a trend of progressive low pressure conditions during fractionations, while the cpx from syenites were formed under increasingly high pressure conditions towards late magmatic differentiations of syenites. This contrasting behaviour of crystallization of cpx in ultramafic and syenitic magmas is worthwhile to discuss. Changes in the activities of SiO_2 and Al_2O_3 in the magma are critical in determining the compositions of cpx⁶. Fractional crystallization trend of ultramafics of the carbonatite complex follows the course of crystallization of alkali basaltic magma with decreasing trends of magmatic pressure and silica activity. At low pressure conditions, cpx show trend towards increasing $Ti+Al^{iv}$ with decreasing Si. A low silica activity (γSiO_2) will favour incorporation of Al in Z sites of cpx. In the analyzed cpx, Si+Al is sufficient to satisfy the numerical requirements of Z group. Incorporation of Ti into cpx structure would be accompanied by Al in Z sites for the rocks formed under low γSiO_2 . According to Yagi and Onuma⁷, a Ti-bearing cpx component may dissolve in considerable amount in diopside molecule. Substitution of Ti^{4+} is invariably involved in the late stages of the ultramafic (alkali basaltic) crystallization, under increasing trend of low γSiO_2 coupled with decreasing trend of magmatic pressure. In contrast, sub-

stitution of Ti^{4+} decreases in or releases out from cpx under decreasing trend of low γSiO_2 coupled with increasing trend of magmatic pressure of agpaitic residual fluid which may be a derivative of alkali basaltic magma. Cpx indicative of crystallization in a high pressure regime are often found in alkali basalts and their derivatives⁸. Further, formation of co-existing phases of melanite and aegirine, greatly affect the chemical content of Ti and Na of associated calcic rich cpx, owing to increase of γSiO_2 in the residual magma. According to Heinrich⁹, Ti content in augite co-existing with melanite is very low. Similarly, a low content of Na is present in fractionated cpx co-existing with aegirine (table 1 cpx - 360). The syenites were formed under silica-saturated alumina poor agpaitic conditions which is evident from their textural features of late crystallizations of mafic minerals subsequent to the crystallization of felsic constituents¹⁰. Thus the last formed mafics have progressively occupied only in the available interstitial places of felsic constituents and hence they were subjected to high magmatic pressure under low temperature and high viscosity conditions².

During differentiation, a phase transformation of cpx into hornblende, biotite, melanite, wollastonite, magnetite, aegirine, calcite or dolomite under favourable environment, resulting in paragenetic accommodation, leads to enrichment of γSiO_2 in residual magma. Increasing of felsic minerals with high γSiO_2 produces a highly viscous residual magma. Rittmann's² parameter $(Or+Ab)^2/(Wo+Hy)$ or i.e. salic/femic constituents for these syenites progressively increases during the differentiation from shonkinite (1.30) to scapolite-melanite syenite (15.82) indicating progressive enrichment of viscosity conditions towards late magmatic stage. In a highly viscous agpaitic magma, cpx crystallize under high pressure conditions even after crystallization of felsic minerals owing to progressive fractional crystallizations of the residual magmas. The high pressure cpx present in syenites of late magmatic fractionates are progressively small in sizes with anhedral or granular form. In thin sections overgrowths of diopside-aegirine, aegirine-melanite, aegirine-wollastonite, wollastonite-para-wollastonite, diopside-calcite and diopside-scapolite are seen. In contrast, cpx from shonkinite, augite syenites and apatite-magnetite-orthoclase-biotite pyroxenite are coarse-grained and euhedral in form and this texture is another evidence for their low pressure geneses.

During differentiation of alkali magma in a closed chamber, magmatic pressure increases owing to concentration of volatiles, immediately over magmatic column and therefore, crystallization takes place under increasingly high pressure conditions. In contrast, crystallization under an open system or during the course of upward migration of a magma causes decreasing trend of magmatic pressure in the residual magma. Under such conditions, low pressure cpx may crystallize. In a closed system, highly Ca-rich cpx are unstable under high P_{CO_2} and they dissociate into calcites, dolomites and some other silicates. Crystallization of melilite instead of Ca-rich cpx may result from magma rich in CO_2 . But under high pressure plutonic conditions, melilites are unstable². Therefore, Ca-rich cpx dissociate into carbonate liquid and a silicate liquid under high P_{CO_2} and t_c^0 conditions. At lower temperatures, a carbonatite magma immiscibly separates out from an alkali silicate magma. On further differentiation of these secondary magmas, comagmatic syenites and carbonatites might be produced. The chemistry and differentiation of Ca-rich cpx from shonkinite seem to link the differentiation trends of ultramafics and syenites and this feature suggests that the parental magma might be of alkali basaltic composition of shonkinitic type from which carbonatitic and alkali syenitic magmas were separated immiscibly at late magmatic stages under high t_c^0 and P_{CO_2} conditions.

Sincere thanks are due to Mr V. K. Garamin, Geochemical Laboratory, Moscow State University, USSR for microprobe analyses.

11 September 1985; Revised 20 January 1986

1. Deans, T. and Powell, J. L., *Nature (London)*, 1968, **218**, 750.
2. Rittmann, A., *Stable mineral assemblages of igneous rocks*, Springer-Verlag, Berlin, 1973.
3. Eriksson, S. C., In: *Crustal evolution of South Africa*, (eds) A. J. Tankard, M. P. A. Jackson, K. A. Eriksson, D. K. Hobday, D. R. Hunter and W. E. L. Minter, Springer-Verlag, Berlin, 1982, p. 424.
4. Ramasamy, R., *Proc. 4th IGS*, Varanasi, 1982.
5. Wass, S. Y., *Lithos*, 1979, **12**, 115.
6. Campbell, I. H. and Boreley, G. D., *Contrib. Mineral. Petrol.*, 1974, **47**, 281.
7. Yagi, K. and Onuma, K., *J. Fac. Sci. Hokkaido Univ.*, 1967, **8**, 463.

8. Binns, R. A., Duggan, M. B. and Wilkinson, J. K. G., *Am. J. Sci.*, 1970, **269**, 132.
9. Heinrich, E. Wm., *The geology of carbonatites*, Krieger, New York, 1980.
10. Saravanan, S. and Ramasamy, R., *Miner. Mag.*, 1971, **38**, 376.

CATALASE ACTIVITY DURING AGEING OF ZAPRIONUS PARAVITTIGER (DIPTERA: DROSOPHILIDAE)

RENU WADHWA, RUPINDER KAUR and S. P. SHARMA

Department of Biology, Guru Nanak Dev University, Amritsar 143 005, India.

THE free radical-induced damage is commonly argued to be the major cause underlying the senescence-related deterioration of body structure and function^{1,2}. Living systems have evolved self-defensive measures, such as antioxidants and antioxidantizing enzyme systems³, to limit the free radical initiated damage to tolerable levels⁴. Catalase (E.C. 1.11.1.6)—a member of antioxidantizing enzyme system, is a heme containing enzyme involved in the metabolism of hydrogen peroxide⁵. The present study delineates the changes in catalase activity in the whole body homogenates of ageing male and female *Zaprionus paravittiger*.

The flies were reared on corn meal agar medium⁶ at $26 \pm 2^\circ C$. Freshly emerging flies were collected at every 24 hr intervals and were transferred to the fresh medium on every 12th day. Age-wise cultures were maintained for 57 days. The mean and the maximum life span is 35 and 70 days for males and 40 and 77 days for females, respectively⁷. Quantitative estimation of catalase was carried out by the method of Aebi⁸. Homogenate (2%, w/v) was prepared by homogenizing 20 mg of the tissue (about 4–5 flies) in 1.0 ml of 50 mM phosphate buffer (pH 7.0). One ml of supernatant obtained after centrifugation of homogenate at 12,000 rpm for 15 min at $4^\circ C$, was added to a mixture of phosphate buffer—50 mM, pH 7.0 (1 ml)—and sodium perborate solution—100 mM, pH 7.0 (3 ml)—preincubated at $20^\circ C$ for 10 min. The reaction was stopped by the addition of sulphuric acid—2 N (3 ml) after 5 min (for stable reading). The remaining perborate was back-titrated with