

a large  $\delta\mu$  and hence large second-order nonlinearities result in these complexes.

The 460 nm band in the neutral ferrocenes is attributed primarily to a d-d transition which shifts to  $\sim 550$  nm on oxidation. The absorption band extends up to  $\pm 50$  nm around  $\lambda_{\max}$  and this may contribute to the resonance enhancement of  $\beta$  through a two-photon mechanism. In the case of complexes containing TCNQ and DDQ, this band may also originate from  $\text{TCNQ}^-$  or  $\text{DDQ}^-$  respectively. Although the  $\lambda_{\max}$  correlates linearly with  $\beta$ , no straightforward correlation between the absorbance at 532 nm ( $\epsilon_{532}$ ) and the measured  $\beta$  is observed. These molecules do not absorb at  $\sim 1064$  nm unlike the mixed valence ruthenium complex<sup>3</sup> and, therefore, a single photon dispersion in  $\beta$  is ruled out.

In summary, we have clearly demonstrated that partially oxidized ferrocenes formed by matching the redox potentials of neutral ferrocene moieties and an oxidant represent an entirely new class of complexes which exhibit large first-order hyperpolarizability.  $\beta$  for the corresponding neutral ferrocenes is, at least, an order of magnitude smaller than the ionic compounds and comparable to other ferrocenyl compounds studied in the past. Since a huge library of metallocenes and their oxidation potentials exist it is possible to design better partially ionic NLO materials based on the above guidelines. We are currently investigating this.

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ACKNOWLEDGEMENTS. We thank Dr S. Ramakrishnan for enlightening discussions. Financial assistance provided by the Department of Science and Technology, Govt of India is gratefully acknowledged.

Received 25 September 1995; revised accepted 16 December 1995

## Occurrence of fluoride in the groundwaters and its impact in Peddavankahalla basin, Bellary District, Karnataka—A preliminary study

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Human diseases associated with excess consumption of fluoride through drinking water and food grains have been observed in many localities in Peddavankahalla basin. Fluorosis is severe in the part of the basin covered by black cotton soil which is under intensive irrigation, comprising six villages. Dental hypoplasia has been noticed in a few villages. We discuss here probable source of fluoride, causes for its concentration and suggest possible remedial measures.

Of the many natural geochemical substances contaminating groundwater, fluoride is most hazardous. Fluoride occurs in minor quantities in groundwater but evokes considerable interest due to its unique character as regards to its impact on physiological system of living beings. This is because very low doses ( $< 1.5$  mg/l) of it promote decay of teeth, whereas when consumed in the ranges  $> 1.5$  mg/l causes fluorosis and related diseases<sup>1</sup>. Preliminary study of the groundwaters of Peddavankahalla basin, Bellary district ( $15^{\circ}05'-15^{\circ}35'N$ ;  $76^{\circ}45'-77^{\circ}05'E$ ) has indicated presence of fluoride in excess of permissible limits in many villages (Figure 1). However, fluorosis is more severe in six villages, viz. Hosahalli, Hagaluru, Karuru, Daruru, Bhairapuram and Koralgondi.

Water samples (34 groundwater and 4 surface water) were collected from Bellary and adjoining villages and analysed for their EC, pH, Ca, Mg, Na, K,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , F, and TDS using standard chemical analytical methods<sup>2</sup>. Fluoride was determined by using an ion selective electrode (models 94-09 and 96-09) with 720 pH/ISE meter (Orion, USA) and the results are presented in Table 1. The analytical results<sup>3</sup> indicate that the groundwaters are weak-to-moderately alkaline and have high concentrations of Na, Cl and TDS. In 22 groundwater samples (64% of the total samples covering 18 villages), fluoride concentration exceeds the permissible limits for drinking water prescribed by ISI and WHO<sup>4,5</sup> (Table 2).

The comparison of fluoride concentration of groundwaters from the shallow dugwells and deeper borewells from the same location has indicated that the deeper aquifers have higher concentration of fluoride than the shallow aquifers.

Gneisses, granites and hornblende schists are the major

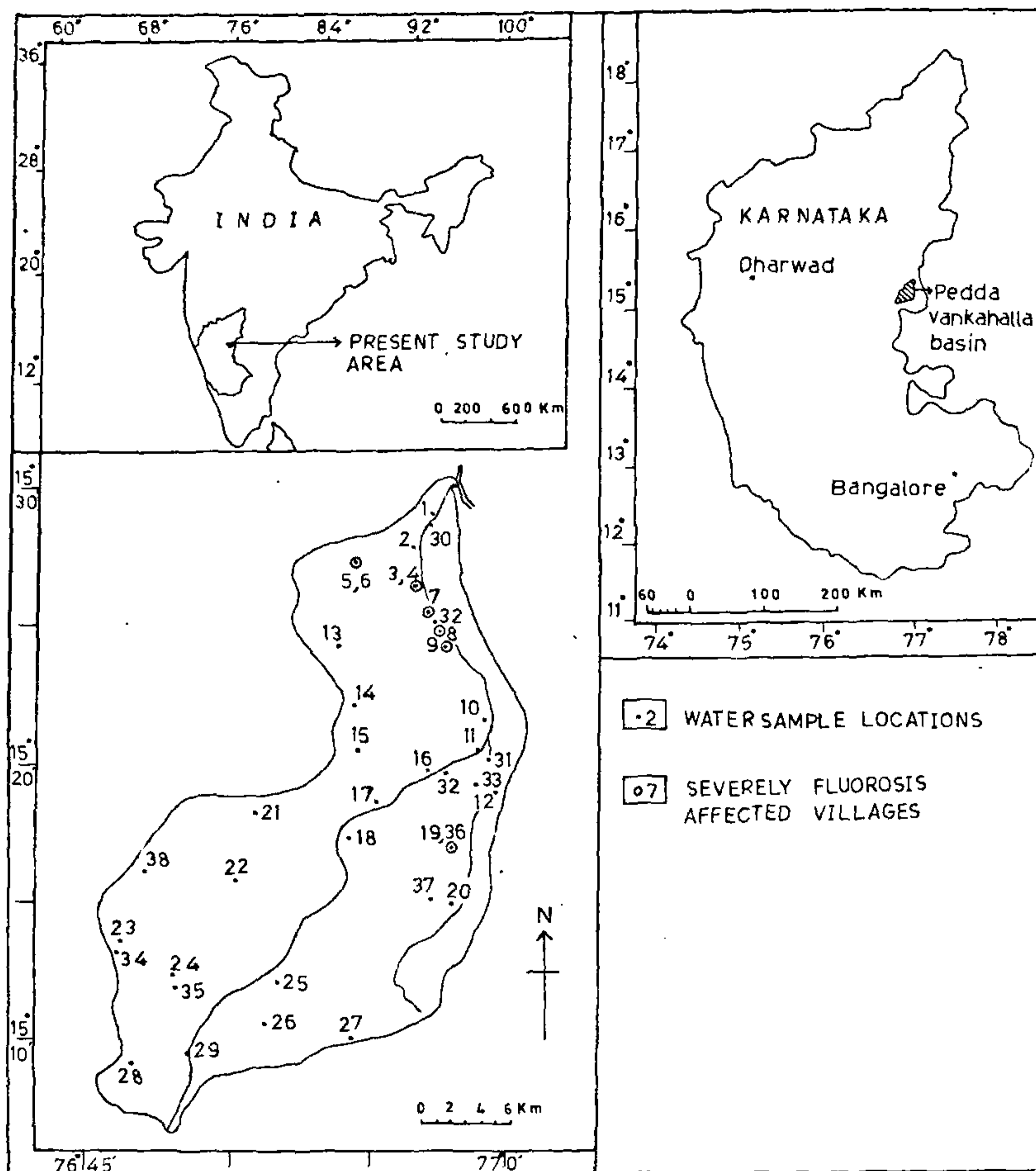


Figure 1. Location map of Peddavankahalla basin.

lithounits of the area. The sources for fluoride in the groundwaters of this area appear to be the fluoride-bearing minerals, viz. apatite (0.4–1.6% of the mode), hornblende (20% of the mode) and biotite (0.5–5% of the mode)<sup>3</sup> (Table 3).

In this region, high degree of weathering and easy accessibility of circulating waters to the weathered rocks due to intensive and long time irrigation are responsible for the leaching of fluoride from their parent minerals present in soil and rocks. Further concentration has been brought about due to the arid climate of the region and long residence time of groundwater in the aquifer.

The influence of local lithology and soil, aided by other factors like very low freshwater exchange due to arid climate of the region (average daily temperature 28°C and average annual rainfall 478 mm) is responsible for higher concentration of fluoride in the groundwater of the region.

The amount of water and consequently the amount of fluoride ingested by living beings is primarily influenced by air temperature<sup>6,7</sup>. According to the USPHS temperature range classification<sup>8</sup>, the study area lies in the range of 25–32°C for which the stipulated upper permissible limit of fluoride is 0.8 mg/l. Fluoride concentration in groundwater from most villages of the region exceeds this upper limit. Therefore, the people from most villages of this region are highly susceptible to the attack of fluorosis any time in future.

Fluorosis is more severe in the canal-irrigated black cotton soil covered area, indicating that in addition to climate, circulation of water by means of irrigation (which aids in leaching of fluoride from soil and weathered rock zone) appears to be a major cause for excess concentration of fluoride in groundwater, and further detailed study on this aspect is under progress.

The pH of the circulating waters is a factor which

**Table 1.** Concentration of fluoride in the groundwater and surface water of the study area

Sample no.	Location	Fluoride (mg/l)
<i>Groundwater</i>		
1.	Buduguppa	6.80
2.	Gosabalu	1.60
3.	Karuru	3.60
4.	Karuru	2.20
5.	Bhairapuram	5.90
6.	Bhairapuram	1.90
7.	Daruru	1.40
8.	Hagaluru	7.80
9.	Hosahalli	6.60
10.	Chananahalu	0.65
11.	Handihalu	2.70
12.	Gudaduru	0.41
13.	Sanavasapuram	2.50
14.	Sindigeri	2.60
15.	Gopalpuram. C	0.71
16.	Kagallu	2.50
17.	Dammuru	1.60
18.	Koluru	1.20
19.	Koralgondi	Erratic
20.	Jalibenchi	3.50
21.	Vaddehatti	0.76
22.	Ereyingalgi	0.33
23.	Kudatini. R.S	1.30
24.	Venivirapuram	2.10
25.	Kolagallu	1.60
26.	Allipuram	0.58
27.	Bellary	1.80
28.	Haraganadona	1.50
29.	Janikunta	2.80
<i>Surface water samples</i>		
30.	P.V. Halla (Buduguppa)	0.46
31.	P.V. Halla (Hagaluru)	0.93
32.	P.V. Halla (Kagallu)	0.30
33.	P.V. Halla (Gudaduru)	0.43
<i>Groundwater samples</i>		
34.	Kudatini	1.20
35.	Venivirapuram	2.50
36.	Koralgondi	2.00
37.	Jalibenchi	4.40
38.	Siddammanahalli	2.60

Analyst: G. Sreenivasan.

**Table 3.** Modal percentage of fluoride-bearing minerals in dominant rocks of the area

Fluoride-bearing minerals	Modal percentage					
	R 9	R 26	R 31	R 36	RC 42(a)	RC 42(b)
Apatite	0.8	0.4	0.5	1.3	1.6	1.5
Biotite	5.4	Ab	0.4	0.1	0.5	Tr
Muscovite	Ab	0.8	Ab	Ab	Ab	Ab
Hornblende	Tr	Ab	Tr	20.4	Tr	Tr

Note: R 9, Grey granite; R 26, Pink granite; R 31, Gneissic granite; R 36, Gneiss; RC 42(a), Gneissic granite; RC 42(b), Gneissic granite; Ab, absent; Tr, Trace.

controls the leaching of fluoride from the fluoride-bearing minerals. The correlation study made and the scatter diagrams plotted on this basis (not presented here) have brought out a positive correlation between the pH and fluoride concentration, indicating that higher alkalinity of the waters promotes the leaching of fluoride and thus affects the concentration of fluoride in the groundwaters.

An urgent need of the region is to take up a detailed diseased victims populistic survey and providing fluoride-free drinking water. As far as possible, the intensive irrigation in black cotton soil-covered region should be minimized by adopting efficient irrigation techniques.

Many defluoridation techniques have been proposed, of which the Nalgonda technique proposed by the NEERI, Nagpur<sup>9</sup>, is cheaper and simple. It involves addition in sequence, bleaching powder, lime and alum to the water. This technique can be easily adapted by villagers at domestic level. In addition to this, the villagers should be educated about the hazards of consumption of fluoride-bearing water and use of simple methods of defluoridation.

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**Table 2.** Comparison of fluoride content of the groundwaters of the study area with Drinking Water Standards

Constituent	ISI (1983)		WHO (1971)		No. of samples exceeding permissible limits	% to the total no. of samples
	Highest desirable	Maximum permissible	Highest desirable	Maximum permissible		
Fluoride	0.6-1.2	1.5	0.5	1.5	22	64*

\*Percentage excludes surface water samples.

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ACKNOWLEDGEMENTS. We thank Prof. M. S. Jagathesan, Department of Geology, A.C. College, Madras for his help in fluoride analysis of water samples. GS is grateful to the authorities, Karnatak University for the award of University Research Studentship.

Received 1 October 1994; revised accepted 13 November 1995

## Australasian microtektites from the Central Indian Basin: Implications for ejecta distribution patterns

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Microtektites belonging to the Australasian tektite strewn field have been recovered in one (SK-16/176) out of three cores examined from the Central Indian Basin. The microtektites have been identified based on their physical appearance, stratigraphic position, chemical composition and geographic occurrence. Their chemistry reveals that among the analysed specimens, a majority belong to the 'normal' microtektite clan, one has a high Mg (HMg) composition shown by bottle green microtektites, and some have an intermediate composition. The absence of microtektites in the other two cores (SK-16/183 and F-2/88B) could be because of the small area of coverage by sediment coring. Therefore, given the vastness of the Australasian tektite strewn field, many more microtektite locations have to be identified in order to arrive at a microtektite distribution pattern.

TEKTITES, which are glassy ejecta generated by impacts, are distributed in large geographic domains called strewn fields. Four such tektite strewn fields occurring in four different geologic and geographic areas are known<sup>1</sup>. Microtektites are small (< 1 mm) glasses found only in the oceans. In three of the four strewn fields, microtektites are present, not only are the boundaries of the strewn fields determined by their occurrence in the oceans, but also mass calculations of the ejecta are carried out<sup>2</sup>. The youngest and also the largest strewn field is the Australasian tektite strewn field encompassing almost the entire Indian Ocean, the land masses from Indochina to Tasmania in the south and also parts of western Pacific Ocean (Figure 1), comprising of a mass of  $10^9$  tons of tektite material<sup>3</sup>. Since the time when Australasian microtektites were first discovered by Glass<sup>4</sup> (identified

based on their physical properties, stratigraphy, geographic location and chemistry) up to 1979, out of the 100 deepsea cores examined, microtektites were found in 33 (ref. 3). At present there are over 40 Australasian microtektite occurrences known<sup>5</sup>. Based on their pattern of occurrence, a possible ray-like distribution was suggested<sup>6</sup>. With the discovery of an iridium anomaly<sup>7</sup>, and shocked minerals<sup>6</sup>, associated with the Australasian microtektite layer, the impact origin of this strewn field is established beyond doubt.

We report here the recovery of Australasian microtektites in one out of three cores investigated which we suggest has significance for the Australasian microtektite distribution.

We examined three deep sea cores, two of which were collected during the 16th Cruise of ORV Sagar Kanya (SK-16/176 Core length: 3.75 m; Lat. 14°00'S, Long. 74°04'E; and SK-16/183 Core length: 4.6 m; Lat. 6°01'S, Long. 76°E) and the third core from the second cruise of MV Farnella (F-2/88B Core length: 0.88 m; Lat. 12°43'S, Long. 77°03'E), (Figure 1). All the cores were previously dated by radiometric<sup>8</sup> and biostratigraphic methods<sup>9,10</sup>, and have ages which extend beyond the 0.77 Ma age of the Australasian strewn field. The cores were sub-sampled at 3 cm interval up to 52 cm core depth, further below at 10 cm interval for SK-16/176; at 5 cm interval for F-2/88B, and up to 100 cm depth for SK-16/183 and, below 100 cm for the latter, the sampling interval was 10 cm. The sub-samples were dried, weighed and wet sieved in a 63 µm mesh sieve and the dried coarse fraction was further dry sieved in 250 and 125 µm sieves. The > 250 µm fractions were scanned using a binocular microscope having a mag-

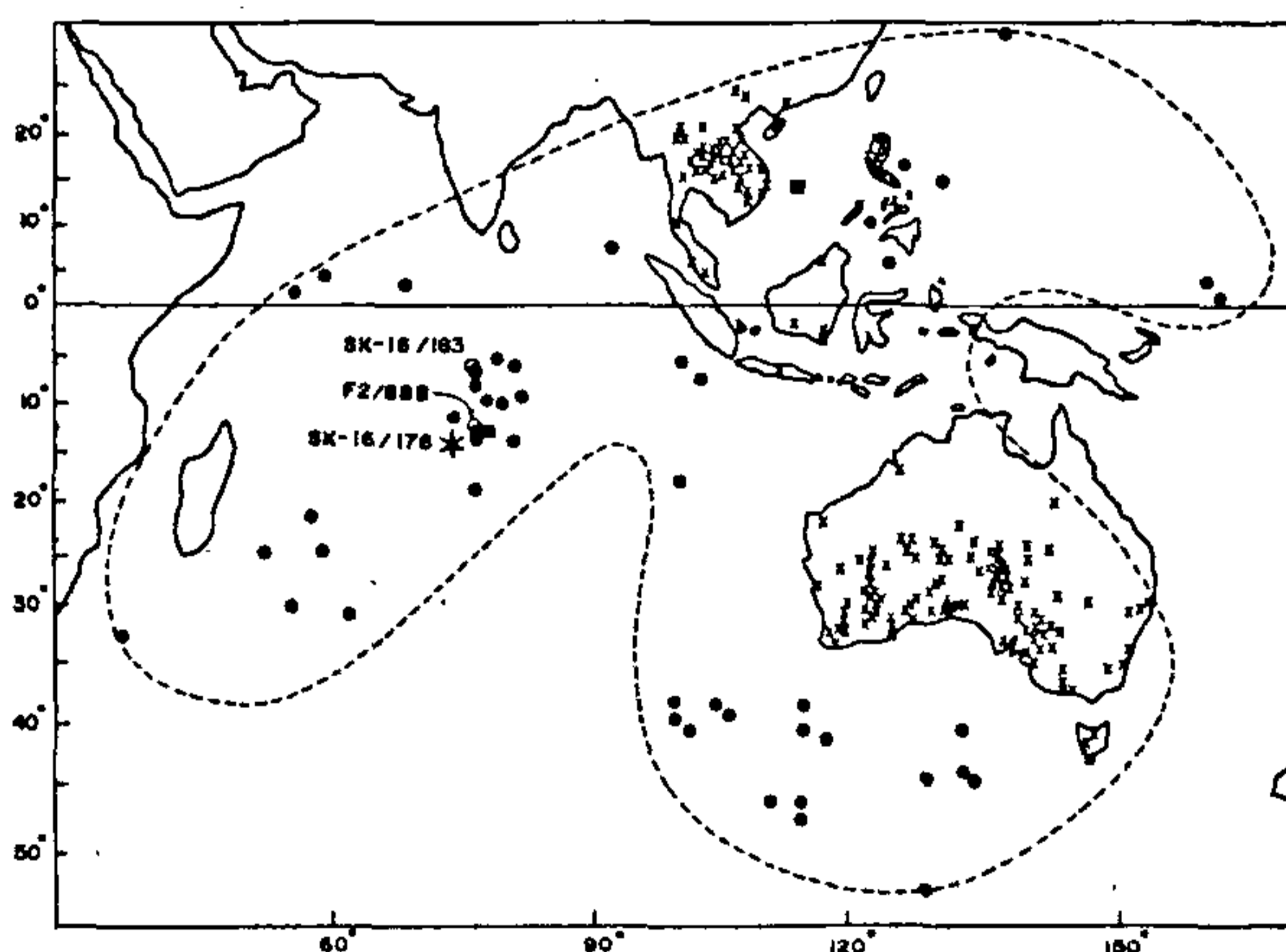


Figure 1. The Australasian tektite strewn field. The dotted lines show boundaries of the strewn field indicating a possible ray-like pattern of distribution<sup>6</sup>. The locations of the three cores (SK-16/176, SK-16/183 and F-2/88B) in this study are marked. The cross marks in the land masses indicate tektite occurrences, the dots in the oceans microtektite occurrences, the squares in the oceans indicate tektite occurrences.