

damage levels has a genetic basis (9). There is apparently continuous selection for defenses in this plant species to reduce leaf area losses.

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- The study site is owned by the Organization for Tropical Studies [G. S. Hartshorn, in *Costa Rican Natural History*, D. H. Janzen, Ed. (Univ. of Chicago Press, Chicago, 1983), pp. 136-141].
- Leaf-cutting ants (*Atta cephalotes*) at La Selva can completely defoliate individuals of *P. arieianum*. Twenty-five randomly selected leaves of each of 25 plants were traced. The tracings were then used to determine occurrence of new damage between five consecutive census periods. Areas of tracings were measured with an electronic area meter (model L1-3050A, LAMBDA).
- All of the leaves from 25 plants were collected. A paper tracing was made of the potential area of each leaf, and the area of the real leaf and the paper leaf were measured with an area meter (7). Individual plants differed significantly in the amount of herbivore damage (analysis of variance, $P < 0.05$, $F = 3.30$).
- Four individuals, selected from four different sites, at least 1 km apart, were cloned. Sixteen clones from each plant were planted at the same understory site in a randomized block design (14 by 14 m). After 14 months, clones differed significantly by genotype in the amount of accumulated herbivore damage (analysis of variance, $F = 3.14$, $P < 0.05$). The mean damage level by genotype for the surviving clones was 9.11, 11.78, 15.34, and 18.01 percent.
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- The method of removal was designed to reduce possible differences in plant response to mechanical versus insect damage [J. L. Capinera and W. J. Roltsch, *J. Econ. Entomol.* **73**, 258 (1980)]. Curculionid weevils [*Peridinetus laetus* Champion, *Peridinetus* sp., and *Ambetes* sp. (D. Whitehead, personal communication)] are major herbivores of *P. arieianum* and produce round to oblong holes, similar in size to those made with a paper punch. I randomly assigned leaves to a damage class (either 0, 10, 20, 40, or 80 percent) and randomly chose the day on which I damaged them. The proportion of an experimental plant's total leaves assigned to each damage class matched the average pattern for naturally damaged plants at a given defoliation level.
- Defoliation pattern within a leaf for a particular damage level was kept constant, as damage distribution within a single leaf can affect photosynthesis rates [F. R. Hall and D. C. Ferree, *J. Econ. Entomol.* **69**, 245 (1976)].
- Small plants, 20 to 33 leaves; medium plants, 34 to 55 leaves; and large plants, 56 to 120 leaves.
- A minimum of 35 plants per treatment was used.
- Analysis of covariance (with original leaf number as the covariate), followed by Tukey means comparison, was performed separately for each

plant size class for the dependent variables, shoot growth and seed production. The growth measurement reported is the total length of new shoots produced over the entire plant. Individuals suffering subsequent appreciable damage, due to further herbivory, or damage due to tree or branchfalls, were omitted from analysis.

- The fruiting structure in *P. arieianum* is a spike of tightly packed, single seeded fruits [W. C. Burger, *Fieldiana Bot.* **35**, 5 (1972)]. Seed output was determined by measuring the length of all infructescences on a plant and multiplying by the mean number of seeds per unit of infructescence.
- Viability was determined by germinating freshly collected seeds in petri dishes with moistened filter paper. The dishes were placed on the forest floor in the understory of primary forest. Mean viabilities and standard deviations of seeds of the first year's fruit crop for the 0, 10, 30, and 50 percent defoliation treatments were 87.43 ± 5.76 , 84.99 ± 63 , 88.22 ± 10.52 , and 54.62 ± 10.98 percent, respectively ($P < 0.01$; Kruskal-Wallis test; $\chi^2(3) = 12.26$).
- The flowering peak of the fully defoliated plants

occurred in April 1982, while that of plants of all lower defoliation levels was in mid-February.

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Elemental Anomalies at the Cretaceous-Tertiary Boundary, Woodside Creek, New Zealand

Abstract. *Iridium and 26 other elements were determined in shale from the Cretaceous-Tertiary boundary at the locus classicus (for iridium anomalies) at Woodside Creek, New Zealand. Iridium, gold, copper, cobalt, chromium, nickel, arsenic, molybdenum, and iron were enriched in the basal 2 millimeters of the 8-millimeter shale parting as compared with the rest of the stratigraphic column. No other shale partings in the column had anomalous concentrations of any element when the data were expressed on a carbonate-free basis. The boundary material showed striking compositional similarities with the Stevns Klint Danish boundary shale. Elemental concentrations were in general much higher in the New Zealand material than in nonboundary shales from elsewhere in the world. The high concentration of iridium (153 nanograms per gram) in the basal layer of the boundary, together with the enrichment of other siderophile elements supports the idea of an extraterrestrial source for much of the material. The iridium/gold ratio of 2.1 is also in accordance with such a source. The iridium content of the basal layer is higher than for any other marine boundary shale obtained on land. The integrated iridium value is 187 nanograms per square centimeter of boundary surface.*

In a benchmark paper, Alvarez *et al.* (1) proposed that mass extinctions at the end of the Cretaceous had been caused by the impact of a large asteroid. As evidence of this, they reported a very large iridium anomaly at the Cretaceous-Tertiary (K/T) boundary in marine shales at Gubbio in northern Italy, Stevns Klint in Denmark, and Woodside Creek in New Zealand. No data were reported from New Zealand beyond the statement that the iridium concentration in the K/T shale was about 20 times that in the adjacent limestone. Alvarez *et al.* (2) later reported an integrated iridium excess of 120 ng cm^{-2} for this site.

Iridium is a siderophile element that is rare in terrestrial material but much more abundant in chondrites and other extraterrestrial bodies. Thus its presence at relatively high concentrations may well indicate an extraterrestrial source for the material studied. The report by Alvarez *et al.* (1) sparked a lively and continuing debate, which resulted in a conference at Snowbird, Utah (3), devoted

entirely to this topic. In the ensuing debate a number of different sources for the iridium anomaly have been proposed: chondritic meteorites or asteroids (4), metal sulfide-cored meteorites (5), comets (6), and terrestrial nonimpaction sources (7-10).

We have determined the elemental content of a suite of marine carbonate rocks from the Woodside Creek section in South Island, New Zealand, in the course of which 27 elements were quantified. The purpose of this work was to determine similarities between the K/T boundary shale of this New Zealand formation and a K/T boundary shale from Denmark, and to compare a variety of shales from other parts of the world with our material in order to determine whether the Woodside Creek material did indeed have an anomalous composition and was not merely reflecting the usual composition of marine shales.

The K/T boundary in the narrow gorge of Woodside Creek in northeastern Marlborough Province, New Zealand, was

originally described by Strong (11). The contact is marked by a disconformity separating thinly bedded siliceous limestones of Teurian age from the more thickly bedded limestone of late Hautaurian (Maastrichtian) age. Fossils diagnostic of a thin layer of lower Teurian rocks (representing perhaps 10,000 years) could not be found, although this does not mean that such a layer is missing. Likewise, an indeterminate thickness of upper Cretaceous strata was not identified. However, if a disastrous terminal event did occur at that time, redissolution or perturbation of the upper Cretaceous layer was to be expected.

We collected a number of rock samples over an interval of 6 m (3.5 m below the boundary and 2.5 m above). The K/T boundary itself was sampled at three intervals within its 8-mm mean thickness. All the samples were limestones except for five shale partings including the K/T boundary material. Figure 1

shows a representation of the stratigraphy as well as the sampling program.

Abundance data for a number of siderophiles that were enriched in the K/T boundary shale, relative to the rocks above and below this interval, are also shown in Fig. 1. Table 1 gives the mean elemental abundances (on a CaCO_3 -free basis) for the K/T boundary at Woodside Creek and for the adjacent Cretaceous and Tertiary limestones. Data are also given for three layers within the boundary itself and are compared with neutron activation values for the basal layer at the K/T boundary at Stevns Klint, Denmark (5). Table 1 also includes our data for nonboundary marine shales.

When the Woodside Creek data were presented in the carbonate-free form to compensate for anomalies that might have arisen as a result of the redissolution of carbonates, small elemental anomalies that would have appeared at the four non-K/T shale partings in the

stratigraphic column were removed.

Chemical analysis was carried out mainly by neutron activation analysis and plasma emission spectrometry (inductively coupled plasma). In the Woodside Creek K/T boundary material, the following elements were enriched (concentrations greater than one standard deviation above the mean of values for the adjacent Tertiary and Cretaceous rocks): aluminum, gold, cobalt, chromium, copper, iron, iridium, and nickel. Sulfur and strontium were depleted in the boundary material. If only the basal layer of the boundary is considered, arsenic and molybdenum may be added to the list of enriched elements. This basal iron-rich layer is a very prominent feature of the Woodside Creek material (as is also true of the basal layer at Stevns Klint). There is a steady rise in siderophiles as one moves down the boundary. This trend is particularly pronounced for chromium and iridium, which increase by a factor of about 6. Other siderophiles (cobalt, gold, iron, and nickel) increase by a factor of 3. The enrichment of arsenic in the basal layer is particularly striking since the concentration increases by a factor of 20.

It is customary to present iridium data on the basis of integrated nanograms per square centimeter of boundary surface in a vertical direction. With an average boundary thickness of 8 mm and a shale density of 3.3 g cm^{-3} , the integrated value for Woodside Creek is 187 ng cm^{-2} compared with 197 for Caravaca, Spain, and 81 for Stevns Klint (2).

Normalization of the iridium content of CaCO_3 -free New Zealand boundary clay to water-free C1 chondrites (580 ng per gram of iridium) gives an extraterrestrial component of 10.4 percent as compared with 21 percent for Stevns Klint and 9 percent for Caravaca.

One of the objectives of our work was to determine whether the K/T boundary shale had elemental concentrations that were truly anomalous with respect to other shales rather than anomalous only in comparison to surrounding carbonate rocks. The mean values for 19 marine nonboundary shales (Table 1) show that many elemental concentrations in the New Zealand material were well above those of nonboundary shales, as in the case of boron, cobalt, copper, chromium, lead, nickel, phosphorus, strontium, tin, and zinc. Sulfur is extremely deficient in the K/T material. It does not therefore seem that the boundary shale has a strong compositional similarity with nonboundary shales.

Our abundance data for the New Zealand boundary shale are similar to mean

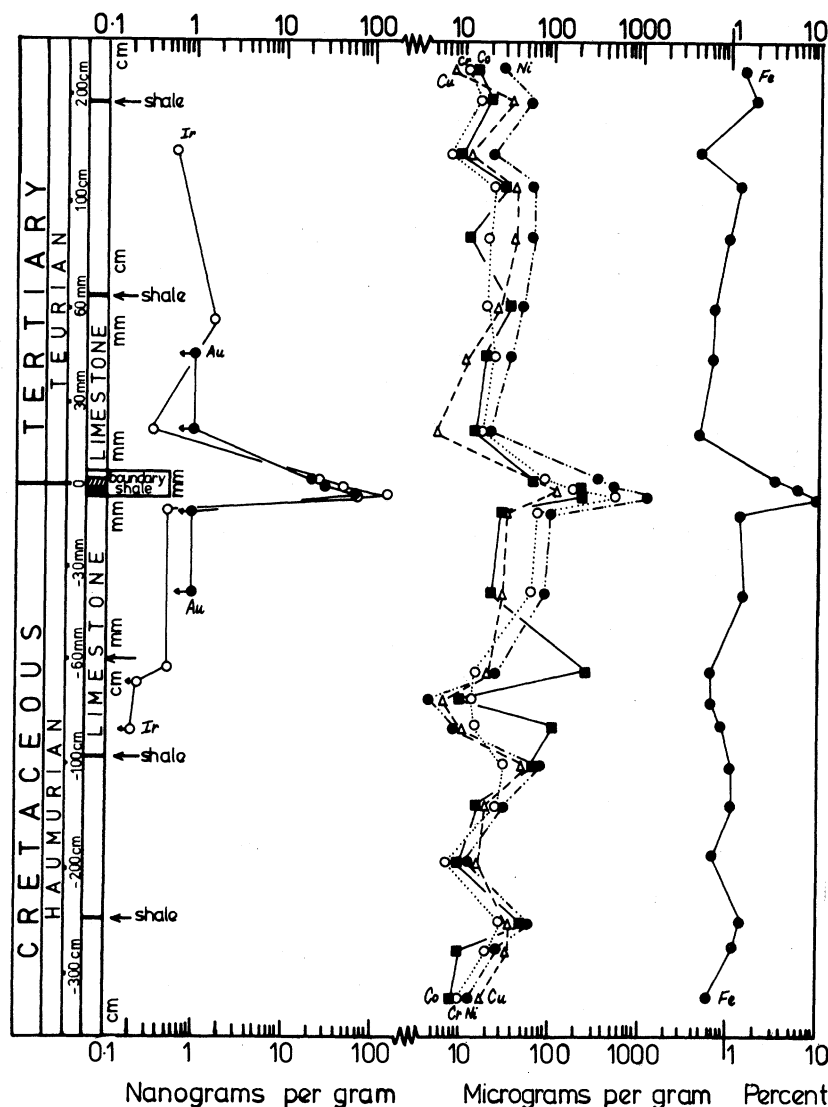


Fig. 1. Concentrations of siderophile elements in the stratigraphic column at Woodside Creek, New Zealand, including the K/T boundary (note different scales along the column).

values reported by Kyte *et al.* (5) for the Stevns Klint K/T material (Table 1). On a carbonate-free basis, there is a striking compositional similarity with the Danish material.

If elemental ratios for Ni/Ir, Ni/Cr, Ni/Co, or Ni/Fe in the basal layer of the New Zealand material are compared with corresponding ratios for the Danish shale reported by Kyte *et al.* (5), it will be noted that there is very good agreement for Ni/Ir and Ni/Cr for the two shales. The values are (New Zealand material first) 6653 and 8333 for Ni/Ir and 1.85 and 2.14 for Ni/Cr.

The New Zealand material has a Ni/Co ratio about half that of Stevns Klint and the value for Ni/As is $\sim 1/6$. The New Zealand shale has an Ir/Au ratio of 2.1 compared with about 6.0 for the Danish boundary shale. Palme (12) has shown that for terrestrial materials an Ir/Au ratio of 0.2 is usual, and that few if any terrestrial sources have ratios exceeding unity. These high Ir/Au ratios are perhaps one of the strongest indications of an extraterrestrial source for some of the material at both K/T boundaries.

The abundance data reported above for the New Zealand K/T boundary shale show an enrichment of the siderophiles cobalt, chromium, gold, iridium, iron, and nickel. There is also concomitant enrichment of the "chalcophiles" arsenic, copper, and molybdenum. It is possible to explain the presence of siderophiles if an extraterrestrial source is assumed, but it is more difficult to account for the enrichment of chalcophiles. Arsenic is usually chalcophilic in the earth's crust and siderophilic in extraterrestrial material. The high concentration of this element in the basal material of the Woodside Creek material could be derived in part from an extraterrestrial source (although in the boundary as a whole arsenic is not significantly enriched). A more likely explanation for this high arsenic concentration is reducing conditions in the ocean at that time, associated with the extinction of plankton and taxa of higher order, or even enhanced volcanism unleashed by violence done to the earth's crust by an impact. A similar mechanism could account for the enrichment of copper and molybdenum.

A number of countervailing arguments have been put forward to account for anomalous concentrations of elements at the K/T boundary. Rampino (10) has suggested that the shale partings have resulted from the dissolution of carbonate material and has proposed that easily weathered chalcophiles precipitate in the clay boundary with its different chemical

Table 1. Elemental concentrations in New Zealand K/T boundary shale from Woodside Creek compared with those in other parts of the stratigraphic column, the basal layer of the Stevns Klint K/T boundary, and nonboundary marine shales (all data expressed on a CaCO_3 -free basis). The data for Stevns Klint are from Kyte *et al.* (5).

Component	New Zealand material from Woodside Creek						Stevns Klint	Non-boundary shales
	Tertiary	K/T boundary				Cretaceous		
		Mean	Top	Middle	Basal			
CaCO_3 (%)	41	7	7	7	7	65	56	8.8
Al (%)	1.99	5.03				2.89		8.6
As ($\mu\text{g/g}$)	25	48	27	74	493	81	86	
Au (ng/g)	<1	42	24	31	71	<1	24	<1
B (%)	0.21	52				0.70		0.017
Ce ($\mu\text{g/g}$)			48	50	49		120	
Co ($\mu\text{g/g}$)	18	125	62	216	216	26	124	20
Cr ($\mu\text{g/g}$)	19	203	87	175	550	19	560	99
Cu ($\mu\text{g/g}$)	23	162				28		52
Fe (%)	0.89	4.05	3.1	4.7	9.6	1.38	6.80	3.50
Ir (ng/g)	<1	70	25	49	153	<1	144	<1
K (%)	0.52	1.13				0.87	1.08	2.10
La ($\mu\text{g/g}$)			32	28	25		128	
Mg (%)	0.37	1.00				0.61		1.20
Mn (%)	0.09	0.07				0.30	0.02	0.09
Mo ($\mu\text{g/g}$)	2.3	3.9	8	31	92	3.1		3
Na (%)	1.73	0.74				3.60	2.72	0.97
Ni ($\mu\text{g/g}$)	32	275	333	515	1018	39	1200	37
P (%)	512	996				1319		359
Pb ($\mu\text{g/g}$)	14	45				31		7
S (%)	0.09	0.04				0.43		0.014
Sc ($\mu\text{g/g}$)			15	15	15		30	
Se ($\mu\text{g/g}$)	16	40				43	68	32
Sn ($\mu\text{g/g}$)	9	10				22		1
Sr ($\mu\text{g/g}$)	521	295				1435		168
Yb ($\mu\text{g/g}$)			2.5	1.8	2.1		8.0	
Zn ($\mu\text{g/g}$)	154	612	328	381	806	171	1200	83
Ni/Ir					6653		8333	
Ni/Cr					1.85		2.14	
Ni/Co					4.71		9.67	
Ni/As					2.06		13.90	
Fe/Ni					96		57	
Ir/Au					2.1		6.0	

and physical conditions. If such were the case, however, the large deficiency of sulfur in the Woodside Creek material would not be expected. A further factor mitigating against the idea that a weathering process is responsible for the accumulation of elements in the K/T boundary is the strong compositional similarity between the New Zealand and Danish material. It is difficult to believe that two clays of such similar composition could have resulted from weathering processes at opposite ends of the earth and at the same time could have produced two equally prominent geochemical signatures of extraterrestrial elements.

A further question to be considered is whether the anomalies at the K/T boundary could have resulted from volcanic activity, which is thought to have been considerable at the time. However, Gilmore *et al.* (13) have pointed out that, among mafic volcanics and plutonic rocks, only dunite contains iridium in significant concentrations (0.83 ng/g in DTS-1 standard dunite). The chromium content of such rocks is of the order of 4000 $\mu\text{g/g}$, which is 24 times that in the

Woodside Creek material and contrasts with an iridium concentration 1/60 of that in the New Zealand material.

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Ultrahigh Pressure: Beyond 2 Megabars and the Ruby Fluorescence Scale

Abstract. A new design of the diamond-window, high-pressure cell has permitted static pressure of 2.8 megabars to be generated for the first time. The design is unusually stable mechanically, and thus it should be possible to use the new cell to study most materials, including hydrogen, in the unexplored pressure region above 1 megabar.

The generation of static high pressures of several megabars for laboratory experimentation has been an important goal for materials science. At pressures exceeding 1 Mbar, the energy equivalent is on the order of the minimum required to convert many materials from insulator

or semiconductor states to the metallic state. Ross and McMahan predicted (1) that hydrogen, for example, would become a high-temperature (greater than 25°C) superconductor at megabar pressures. In the present study new designs of high-pressure apparatus have been

used successfully in maintaining ruby-plus-metal composite samples stably at 2.8 Mbar without apparatus failure. This result constitutes a major advance over the earlier maximum, which was limited to 1.7 Mbar (2).

The quest to reach megabar pressures in order to observe metallic and other behavior of materials has benefited from the use of apparatus in which single-crystal diamonds are integral, strong component parts. Diamonds have served as windows for radiation transmitted and emitted in interactions with samples held under pressure (2). The ability to study a pressurized sample in situ by spectroscopic methods has been crucial in modern high-pressure research.

The ultimate strength of diamonds at very high pressures has become a major design consideration. Analysis of the diamonds that flowed and those that did not flow under the same experimental conditions in other experiments suggested that impurity levels of nitrogen inclusions could be important (2). Some diamonds contain ~700 parts per million of nitrogen. Diamonds in which nitrogen platelets were present, as determined by high-sensitivity Fourier-transform infrared analysis (3), were selected for the

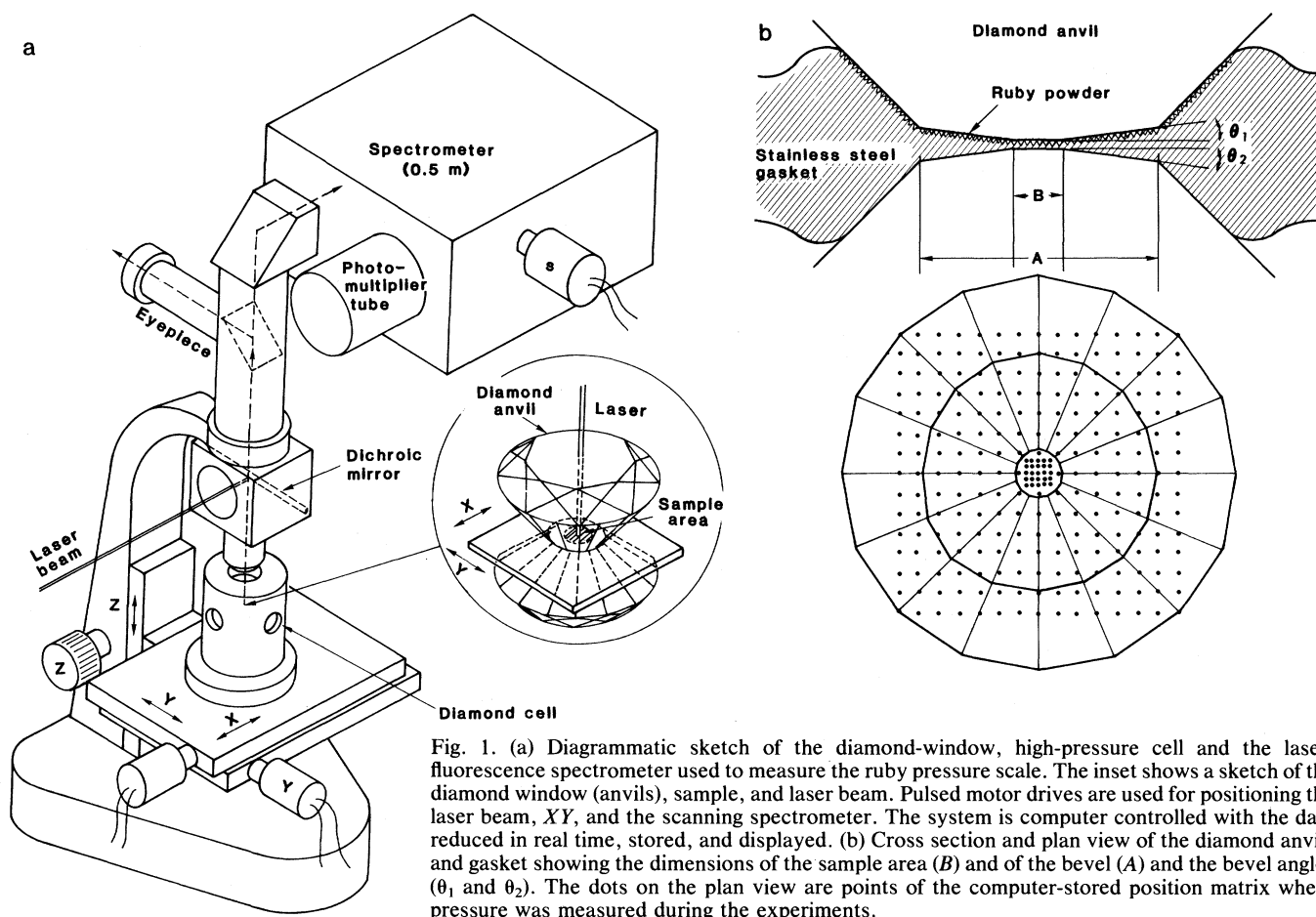


Fig. 1. (a) Diagrammatic sketch of the diamond-window, high-pressure cell and the laser-fluorescence spectrometer used to measure the ruby pressure scale. The inset shows a sketch of the diamond window (anvils), sample, and laser beam. Pulsed motor drives are used for positioning the laser beam, XY, and the scanning spectrometer. The system is computer controlled with the data reduced in real time, stored, and displayed. (b) Cross section and plan view of the diamond anvils and gasket showing the dimensions of the sample area (B) and of the bevel (A) and the bevel angles (θ_1 and θ_2). The dots on the plan view are points of the computer-stored position matrix where pressure was measured during the experiments.