Chapter 1 General Introduction

1.1 Introduction

This thesis incorporates three major components with emphasis on three different types of geomaterials: deep-sea ashes, dropstones and xenoliths concerning the theme of geochemical evolution of crust-mantle system in Proterozoic and/-or Cenozoic in the circum-Pacific region: 1. the Izu-Bonin-Mariana (IBM) arc-backarc system, western Pacific; 2. Kurile-Kamchataka-Aleutians (KKA), northern Pacific, and 3. the San Francisco Volcanic Field (SFVF) located on the southwestern margin of the Colorado Plateau. The three parts are:

1). Geochemical evolution of the Izu-Bonin-Mariana (IBM) arc-backarc system: evidence from deep-sea volcanic ashes recovered by Deep Sea Drilling Program (DSDP) Leg 60 and Ocean Drilling Program (ODP) Leg 125 in the IBM forearcs, western Pacific;

2). Geochemical and isotopic characteristics of lower crustal xenoliths derived from the San Francisco Volcanic Field (SFVF), northern Arizona, USA;

3). Provenance of Pliocene-Pleistocene dropstones (ice-rafted debris) recovered on ODP Leg 145, northern Pacific Ocean.

My emphasis in the main part of this thesis is the volcanic ash study because there are limited published geochemical studies on these materials whereas relatively extensive xenolith studies have been reported (e.g., Dawson et al., 1986; Nixon, 1987; Vielzeuf and Vidal, 1990; Fountain, Arculus and Kay, 1992). Therefore, "Geochemical evolution of the Izu-Bonin-Mariana (IBM) arc-backarc system: evidence from deep-sea volcanic ashes recovered by DSDP Leg 60 and ODP Leg 125 in the IBM forearcs, western Pacific" is chosen as the thesis title. "Geochemical and isotopic characteristics of lower crustal xenoliths derived from the San Francisco Volcanic Field (SFVF), northern Arizona, USA" and "Provenance of Pliocene-Pleistocene dropstones (ice-rafted debris) recovered on ODP Leg 145, northern Pacific Ocean" are included in Appendix 8 and Appendix 9, respectively. The paper "Geochemical evolution of arc systems in the western Pacific: the ash and turbidite record recovered by drilling" is also presented in Appendix 10. In addition, the data of Yasur volcanic ashes are given in appendix 7. A related publication list completed during my doctoral studies is presented in Appendix 6. Detailed information about sample locations, sample selection and description, analytical techniques and all data for IBM volcanic ashes, xenoliths and dropstones studied are given in Appendices 1 to 5. References include all cited publications from the main text and appendices.

1.2 Why the IBM arc-backarc system?

The geological and tectonic setting of the IBM arc-backarc system and previous extensive studies on the volcanic rocks and ashes of the Philippine Sea Plate (see Chapter 2) provide a unique opportunity for studying the geochemical evolution of this system for the following reasons:

1). The IBM arc-backarc system appears to have been built upon oceanic crust. Therefore, assimilation of continental crust or sediments is unlikely to play a major role in determining the compositions of the erupted materials.

2). There are detailed age studies of the Philippine Sea Plate, which was formed by at least three successive arc building and backarc spreading phases. This is an excellent framework for studies of island arc evolution.

3). Extensive studies of the geology, tectonics and geochemistry of the Philippine Sea Plate have been published. Therefore, there are a large amounts of geochemical data available for comparative studies.

4). The collected volcanic ash samples span almost the whole evolution history of the IBM arc system from about 42 Ma B.P. to present. Furthermore, a number of advanced analytical techniques can be used to obtain a large body of integrated elemental abundance and isotopic data.

1.3 Problems of the IBM arc system

There are extensive studies on the IBM arc-backarc basin system as briefly reviewed in Chapters 2 and 3. The IBM arc-trench system is a type intraoceanic system with which other older or less well-studied systems can be compared (Taylor, 1992). Because of sampling difficulties (the entire IBM area is mostly submerged and the islands are of restricted area) and the limitation of separate studies, however, many problems remain controversial or unsolved in our understanding of the IBM arc system. For instance: - 1. are basalts or andesites the predominant magma types? 2. what are the protolith (s) of primary arc basalts: high-alumina basalts (HAB) or high-magnesium basalts (HMB)? 3. is the genesis of the spectrum of arc volcanic compositions dominated by fractional crystallisation or magma mixing or any other processes? 4. are there any along- and /or across- arc geochemical variations and, if so, what is their cause? 5. are there any temporal changes in the geochemistry of arc magmas and, if so, what is their cause? 6. can we detect crustal growth using geochemical parameters believed to correlate at least globally with crustal thicknesses? 7. is there inter-arc synchroneity of major periods of explosive activity? 8. do episodes of major explosive activity in arcs correlate with climate change? 9. what, if any, components from the subducting slab are involved in arc magma genesis? 10. can we identify an agent of mass transfer between subducting slab and mantle wedge, e.g., is this a direct partial melt or hydrous fluid derived from slab dehydration reaction? 11. is there a common mantle source under the Philippine Sea Plate, N-MORB type mantle or ocean island basalts (OIB) type mantle? 12. what is the relationship among IAB (island arc basalts), OIB and mid-ocean ridge basalts (MORB) on the basis of their occurrence and geochemical characteristics?

1.4 Scope and Organisation of this study

Studies of volcanic ashes derived from the IBM arc system provide another useful way to understand IBM arc volcanism as discussed in Chapter 3. It is beyond the scope of this thesis to tackle all the problems mentioned above. However, a systematic study using various techniques and approaches on a complete set volcanic ash samples may provide important insights into the geochemical evolution of IBM arc system. Following are the main objectives of this study: 1) to review the geochemical studies of deep-sea volcanic ashes and evaluate their significance with respect to arc volcanism; 2) to systematically characterise major element variations of individual glass shards and mineral crystal fragments from homogeneous and heterogeneous ash layers; 3) to attempt to characterise representative trace element (e.g., Rb, Ba, Sr, Zr, and Y) variations of individual glass shards from homogeneous and heterogeneous ash layers; 4) to characterise a complete set of trace element variations of bulk ashes; 5) to attempt to extract magmatic Sr and Nd isotopic ratios and the most incompatible element ratio - Ba/Rb values, and assess the importance of subducted sediments and altered oceanic crust; 6) to systematically compare IBM volcanic ashes with IBM volcanic rocks and MORB, and to discuss their similarities and differences; 7) to synthesise all the available element and isotopic data from the IBM region and to constrain models for the geochemical evolution of this arc-backarc basin system; and 8) to discuss the possible relationships among the IAB, OIB and MORB.

In order to achieve these objectives, 184 volcanic ash layers recovered from DSDP Leg 60 Sites 458 and 459B and ODP Leg 125 Sites 782A, 784A and 786A have been studied (see Appendix 1). About 1753 individual glass shards from these ash layers were analysed for major elements by energy dispersive spectrometry-electron microprobe analysis (EDS-EMP); about 220 individual glass shards drawn from this set were analysed for selected trace elements Rb, Ba, Sr, Zr, Y, Ni, Cu, Zn, Ga using proton-induced X-ray emission-proton microprobe (PIXE-PMP); approximately 2400 individual mineral shards of plagioclase, clinopyroxene, orthopyroxene, Fe-Ti oxides, olivine and rare minerals such as amphibole and K-feldspar were analysed by EDS-EMP; 45 representative (30 homogeneous and 15 heterogeneous) bulk ash layer samples were selected for Sr and Nd isotopic ratio determination; and 29 representative (24 homogeneous and 5 heterogeneous) bulk ash layer samples and 6 representative pure bulk glass samples were analysed for trace elements (including REE) by Inductively Coupled Plasma Source Mass Spectrometry (ICP-MS). The results are presented and discussed as follows:

Detailed information about sample location, sample selection and description, analytical techniques and all data are presented in Appendices 1 to 3. Chapter 2 summarises relevant aspects of the geology, geophysics, tectonics and geochemistry of the Philippine Sea Plate. Chapter 3 briefly reviews the nature and occurrence of deep-sea volcanic ashes, samples from island arcs and specifically volcanic ash studies of the IBM arc system. Chapter 4 presents the major element chemistry of individual glass shards from ash layers. The mineral chemistry of individual phenocrysts from ash layers is presented in Chapter 5 and selected trace element geochemistry of individual glass shards in Chapter 6. Chapter 7 documents the trace element geochemistry of representative bulk ashes and bulk glasses. Chapter 8 presents Sr-Nd isotope data for the volcanic ashes and discusses their significance. Also, examples of the most incompatible element (Ba and Rb) abundances of arc magmas, mantle sources and oceanic sediments are reviewed and discussed. Chapter 9 discusses the possible provenances of volcanic ashes, petrogenesis of IBM volcanic ashes and geochemical evolution of IBM arc-backarc system. Generic problems of ash studies and possible directions for future ash studies are described in Chapter 9.

Chapter 2 Geological, Tectonic and Geochemical Framework of the Philippine Sea Plate

2-1 The tectonic and geological setting of the Philippine Sea Plate

The Philippine Sea Plate (Figure 2-1) is bounded on the east, southwest and northwest by a system of convergent margins including the Izu-Bonin, Mariana, Yap, Palau, Philippine, Ryukyu and Nankai trenches. The plate is one of several small western Pacific plates that originated approximately 45 Ma ago during a phase of plate reorganisation associated with the NNW to WNW change in motion of the Pacific tectonic plate (Clague and Jarrard, 1973). The Philippine Sea plate, which was formed at least by three successive arc building and backarc spreading phases, is divided into two parts by the N-S trending Palau-Kyushu Ridge (PKR). The western part consists of the West Philippine Sea region (Watts et al., 1977; Mrozowski et al., 1982); the eastern part mainly consists of the Izu-Bonin-Mariana (IBM) arc-backarc region (e.g., Fryer, Pearce, Stokking, et al., 1990b). The oldest part of the Philippine Sea plate underlies the West Philippine basin and is bounded by the Nankai and Philippine trenches and the Palau-Kyushu Ridge. Prominent topographic features in this area include the Daito Ridge, Oki-Daito Ridge and Daito Basin, the Central Basin Ridge and the Benham Rise. The present-day tectonic configuration of the IBM arc-backarc region comprises (from east to west): the Izu-Bonin and Mariana trenches; the Bonin and Mariana forearc terrane; the active Izu-Bonin and Mariana island arcs; the actively spreading Mariana backarc basin (Mariana Trough) or, in the case of the Izu-Bonin region, the incipient rift basins of the Izu-Bonin backarc (IB Rifts); the West Mariana Ridge (WMR), a remnant arc; the Parece Vela and Shikoku marginal basins; the Palau-Kyushu Ridge (PKR), the westernmost remnant arc. Subduction of Cretaceous Pacific oceanic lithosphere is currently taking place at absolute velocities between 8 and 10 cm/year to the northwest; the subduction angle is about 12° at shallow depths, steepening in some parts of the Mariana system to nearly vertical below about 100 km (see Fryer, Pearce, Stokking, et al., 1990b). Numerous studies show that these basins in the eastern part of the Philippine Sea plate may have been formed by successive episodes of opening from west to east (Karig, 1971a,b, 1975; Seno and Maruyama, 1984).

The Daito and Oki-Daito Ridges and Daito Basin form the oldest section of the Philippine Sea plate and have been interpreted as an arc-backarc basin complex formed along a southwestward dipping subduction zone (Karig, 1975; Seno and Maruyma, 1984). The Central Basin Ridge is an extinct spreading centre that was active between 60 and 40 Ma. The ridge may have been a backarc spreading centre associated with the northern Palau-Kyushu, Daito and Oki-Daito arcs (Karig, 1975; Seno and Maruyma, 1984). The Benham Rise has been interpreted as section of a single oceanic plateau that formed along the Central Basin Ridge at 45-50 Ma and was subsequently rifted by spreading at the Central Basin Ridge (Hilde and Lee, 1984).

The Palau-Kyushu Ridge (PKR) was formed by westward dipping subduction of the Pacific plate between 44 and 29 Ma (Scott et al., 1980; Meijer et al., 1983). Starting at approximately 30 Ma, the Ridge was rifted by backarc spreading that formed initially the Parece Vela and then the Shikoku basins. Volcanic rocks of this arc were recovered from DSDP Leg 59 Site 448 drilled on the submerged PKR, and in several locales displaced toward the modern Mariana Trench: the Mariana Islands of Guam and Saipan and the submerged Mariana forearc (DSDP Leg 60 Sites 458 and 459) (Figures 2-1 and 2-2). Evidence for two episodes of volcanic activity (summarised by Ingle, 1975) is present on Guam. The first is an older, tholeiitic episode (Alutom formation) that lasted from at least 42 Ma to about 34 Ma. Only sporadic volcanism was recorded between 30 and 25 Ma. After a lull in arc volcanism, a second period of volcanic activity occurred on Guam between 16 and 13 Ma. This period of volcanism has calc-alkaline affinities and is recorded in the upper Facpi volcanic formation (Stark, 1963; Tracey et al., 1964). No record of more recent arc volcanism exists on Guam. Saipan has a similar record of activity (Cloud et al., 1956; Schmidt, 1957). Only the older suite occurs on Tinian where 42 to 37 Ma old pyroclastic deposits have been found (see Scott, 1983).

The Parece Vela Basin, to the east of the PKR, opened after waning of the volcanism on the PKR (Karig, 1975). Mrozowski and Hayes (1979) used magnetic anomalies to show that the opening of the central part of the basin occurred between 30 and 17 Ma. The Shikoku Basin opened somewhat later, between 25 and 17 Ma (Shih, 1980). Basin magmatism eventually gave way to arc volcanism along the West Mariana and the IwoJima ridges, which continued from 20 to 9 Ma (Scott et al., 1980). The Parece Vela and Shikoku basins were explored on DSDP Leg 58 (Sites 442-444 in the Shikoku basin) and Leg 59 (Sites 449 and 450 in the Parece Vela basin).

It was not until about 20 Ma ago that the West Mariana Ridge (WMR) became a source of volcanic material (Rodolfo, 1980). Late Pliocene strata from Guam and from the West Mariana Ridge (Karig and Glassley, 1970) contain abundant montmorillonite or volcanic glass (or both), indicating ash-fall activity during that time. The pumice recovered from the dredge hauls on the West Mariana Ridge indicates shallow water or subaerial eruptions (Karig and Glassley, 1970) and implies that subsidence occurred after cessation of the late Pliocene dacitic volcanism. Vesicular silicic volcanic rocks collected along an 800 km length of the West Mariana Ridge seem best explained as analogous to contemporary volcanism in the western Izu-Bonin arc system (Figure 2-3). On the islands of Niijima and Kozushima, rhyolitic lava domes, pumice cones, and flows of very vesicular and silicic lava (Tsuya, 1937; Kuno, 1962) occur almost exclusively. The silicic volcanism in the Izu-Bonin-Mariana arc system seems to accompany the initial stage of inter-arc basin development (Karig, 1971a,b).

The modern Izu-Bonin-Mariana (IBM) arc-backarc system formed by the subduction of the Pacific plate beneath the Philippine Sea plate extends about 2400 km from north (Oshima, Japan) at 35°N to south (Guam) near 13°N (Figures 2-1 to 2-3). This system is neither simple in terms of present structure nor without petrologic complexity. In the north it is known as the Izu arc, from Oshima to Nishinoshima, and includes numerous volcanic islands; the Bonin arc (also referred to as the Volcano arc, Simkin et al., 1981; Bloomer et al., 1989a,b) extends from Nishinoshima near 27°N to Minami-IwoJima at 24°N. Collectively, the Izu and Bonin arcs are termed the Izu-Bonin (or Ogasawara) Arc, which is about 1200 km long extending from Oshima to Minami-IwoJima islands, and about 400 km wide, being comparable with the Honshu Arc of Japan (Yuasa et al., 1991). It continues southward to the Mariana Arc. From west to east, the Izu-Bonin arc consists of the Nishi-Shichito, Shichito and Bonin Ridges. The Shichito Ridge includes both subaerial and submarine edifices (Honza and Tamaki, 1985; Yamazaki et al., 1991). This Ridge is divided into two parts, northern and southern parts, by the Sofugan Tectonic Line (Yuasa, 1985). Five very young backarc basins (rifts): Hachijo, Myojin, Sumisu, Torishima, and Nishinoshima, extensional in origin, are forming behind the volcanic front in the northern part of the Izu-Bonin arc (Karig, 1971a,b; Tamaki et al., 1981; Ikeda and Yuasa, 1989). No active backarc basins (depressions) (Tamaki et al., 1981) are recognised between Nishinoshima and Minami-IwoJima. Tamaki et al. (1981) suggested that this part of the arc has a tectonic setting similar to a Chilean-type arc with no backarc spreading because of collision of the Bonin (Ogasawara) plateau with the Izu-Bonin arc.

Yuasa (1992) discussed the origin of along-arc geologic variations on the volcanic front of the Izu-Bonin Arc. He suggested that the two segments (north and south) were originally independent arcs that developed differently and are now joined. The northern arc was produced first at 48 Ma by subduction of the Pacific Plate under the northern part of the Palau-Kyushu Ridge from the north before opening of the Shikoku and Parece Vela basins. The southern arc was produced by subduction of the same plate from the east after the change of plate motions of ~ 42 Ma. A wedge of oceanic crust due to opening of the Parece Vela Basin broke in between the northern and southern parts of the Izu-Bonin arc. The thermal structure of the mantle beneath the northern part is believed to be different from the southern part. Partial melting of the mantle in the north is probably more extensive and at lower pressures than in the south (Yuasa, 1992). The Izu-Bonin arc is split at 24°N into the inactive or remnant West Mariana Ridge and the active Mariana Ridge, as a result of the opening of the Mariana Trough at ~ 5 Ma (Hussong and Uyeda, 1981). The volcanoes of the Shichito Ridge region may be as old as 20 Ma and postdate the opening of the Parece Vela and Shikoku basins; those of the Mariana arc are inferred to postdate the opening of the Mariana Trough (deVries Klein and Kobayashi, 1980). For the Izu-Bonin arc, the volcanic front is about 200 km from the trench and 125-150 km above the Benioff zone (Isacks and Barazangi, 1977).

Similarly, the Mariana system has an intricate history. The Mariana active arc can be divided into three provinces based on the geographic distribution of submarine and subaerial volcanic islands and seamounts (Dixon and Stern, 1983; Stern et al., 1984, 1989) (Figure 2-3). The Northern Seamount Province (NSP), from 24°N to 20°30' and the Southern Seamount Province (SSP), from 16°30' to Tracey Seamount at 13°20', are entirely submarine, whereas the Central Island Province (CIP), from Uracas at 20°30' to Anatahan at 16°30', is largely subaerial but includes some submarine volcanoes termed as CSP (e.g., Bloomer et al., 1989a,b). Most of the edifices in the arc are constructed upon the juncture of older frontal arc crust and back-arc basin crust (Hussong and Uyeda, 1981; Bloomer et al., 1989a). In both the CIP and NSP there are small chains of volcanos extending into the backarc basin from some of the edifices along the main magmatic front (Hussong and Fryer, 1983; Bloomer et al., 1989a). These "cross-chains" may be associated with fractures or transforms in the backarc crust (Hussong and Fryer, 1983). The volcanoes of the modern IBM arc-backarc system are situated about 100-150 km above the Wadati-Benioff Zone (e.g., Katsumata and Sykes, 1969).

2-2 The volcanological and geochemical features of the Philippine Sea Plate

The Philippine Sea plate seafloor was explored by the Deep Sea Drilling Project (DSDP Legs 6, 31, 58, 59 and 60) and Ocean Drilling Project (ODP Legs 125 and 126) (Fischer, Heezen, et al., 1971; Karig, Ingle, et al., 1975; deVries-Klein, Kobayashi, et al., 1980; Kroenke, Scott, et al., 1980; Hussong, Uyeda, et al. 1981; Fryer, Pearce, Stokking, et al., 1990a, 1992; Taylor, Fujioka, et al., 1990, 1992) in addition to numerous dredging programs. The eastern part of the plate was one of the type areas utilised by Karig (1975) in the development of the concept of backarc basin formation. Similarly, the volcanically active eastern convergent margin, especially the modern Izu-Bonin-Mariana arc-backarc region, is widely cited as a classic example of an intra-oceanic island arc (e.g., Meijer, 1976; Stern and Ito, 1983; Woodhead and Fraser, 1985; Woodhead, 1988, 1989; Lin et al., 1989, 1990).

Backarc basin basalts were erupted in the West Philippine basin during the 65-40 Ma period, the Parece Vela and Shikoku basins during 32-17 Ma, and the Mariana Trough from 5 Ma to present (Hussong and Uyeda, 1981), and are beginning to be erupted at the Sumisu Rift and other Izu-Bonin rifts (Ikeda and Yuasa, 1989; Fryer et al., 1990; Hochstaedter et al., 1990a,b; Stern et al., 1990; Ikeda et al., 1992). All these backarc basin basalts have compositions that are either similar to MORB (West Philippine, Parece Vela, Shikoku, and Mariana Trough) or transitional between MORB and island arc tholeiites (Mariana Trough north of 18°N and Izu-Bonin Rifts) in terms of trace element and mineral characteristics and Sr-Nd isotopic values (Volpe et al., 1987, 1990; Ikeda and Yuasa, 1989; Fryer et al., 1990; Hochstaedter et al., 1990a,b; Stern et al., 1990; Hickey-Vargas, 1991; Ikeda et al., 1992; Stolper and Newman, 1994). The coherence of these basins indicates that the sources of Philippine plate basin magmas have changed little over the past 60 Ma (Hickey-Vargas, 1991).

Numerous geochemical studies have been directed toward an understanding of the youngest portion of the Philippine Sea plate, including the volcanically active Izu-Bonin-Mariana arc, the Mariana Trough, and the Izu-Bonin Rifts. The volcanoes of the CIP have received particular attention (Meijer, 1976, 1982; DePaolo and Wasserburg, 1977; Dixon and Batiza, 1979; Stern, 1979, 1981; Nohda and Wasserburg, 1981; Meijer and Reagan, 1981a, 1983; Stern and Ito, 1983; Hole et al., 1984; White and Patchett, 1984; Woodhead and Fraser, 1985; Ito and Stern, 1986; Woodhead et al., 1987; Woodhead, 1988, 1989). The volcanoes are erupting basalt-to-dacite lavas of both the tholeiitic and calc-alkaline series. There is a general recognition that the incompatible element and isotopic ratios show remarkably little variation from volcano to volcano (e.g., Dixon and Batiza, 1979; Chow et al., 1980; Stern, 1981,1982; Stern and Ito, 1983), but controversy persists regarding the sources involved in magma generation. This argument concerns the relative roles played by the subducted lithosphere and sediment (e.g., Kay, 1980; White and Patchett, 1984; Hole et al., 1984; Woodhead and Fraser, 1985; Woodhead, 1989; Stolper and Newman, 1994) as opposed to that of the mantle wedge (e.g., Meijer, 1976; DePaolo and Wasserburg, 1977; Stern, 1981; Stern and Ito, 1983; Ito and Stern, 1986).

Most studies of intraoceanic arcs have concentrated on subaerial edifices because of their size and accessibility. The subaerial volcanic rocks, however, make up only a small part of volume of material erupted in these arcs; over 90% of the material in arcs such as the Marianas or Tonga is erupted in a submarine setting (Bloomer et al., 1989a). Over half the length of the presently active Mariana arc is represented only by submarine volcanoes (Stern et al., 1989). Therefore, studies have extended to include submarine volcanoes. The SSP has been described by Dixon and Stern (1983), Stern and Bibee (1984) and Stern et al. (1989) and has erupted basalts, basaltic andesites, and dacites. The submarine volcanos of the NSP have also been described in detail (Garcia et al., 1979; Wood et al., 1981; Stern et al., 1988; Bloomer et al., 1989a,b; Lin et al., 1989, 1990; Jackson, 1991; Stern et al., 1993). The results of recent efforts to sample all of the submarine volcanoes along the magmatic front of the Mariana arc have led to some surprises. Lavas from the

NSP show greater compositional variability than that seen in the CIP, including variation in mineralogy, major and trace element chemistry, and isotopic compositions, while the geochemical features of lavas from the SSP are similar to those from the CIP. Lavas from the SSP are as evolved as those from the large CIP edifices (e.g. Dixon and Stern, 1983; Stern and Bibee, 1984).

Most of the andesitic lavas in the SSP and CIP result from low-pressure crystallisation of a mantle-derived basaltic magma (Stern, 1979; Meijer and Reagan, 1981a). Dixon and Stern (1983) have suggested that a few of the lavas in the SSP may have been derived from dacitic parental melts. The inter-element variations of samples within and between edifices suggest that crystal-liquid fractionation may be an important control in the variation of lava composition within the Mariana arc (Bloomer et al., 1989b). The element variations are consistent with extraction of mixtures of olivine, pyroxene, and plagioclase. In contrast to the predominantly basaltic CIP, southern NSP edifices contain abundant hornblende andesites and more felsic lavas, with modest enrichment in LILE and LREE (Bloomer et al., 1989b). Lavas from the northern NSP are approximately saturated in silica, contain atypical phenocryst assemblages (including biotite in some cases), and have strong enrichment in LILE and LREE (Stern et al., 1988; Bloomer et al., 1989b). The strong enrichment observed in northern NSP lavas, however, are accompanied by lower values of certain elemental ratios typically thought to be diagnostic of arc lavas (i.e. Ba/La and Sr/Nd; Lin et al., 1989).

The lavas of the northern NSP and IwoJima region can be divided into two groups based on their bulk chemical compositions. An alkalic group (Irvine and Baragar, 1971), characterised by high K_2O/Na_2O (0.4-1.2) showing strong shoshonitic affinities with phenocrysts of plagioclase, clinopyroxene, olivine and biotite (Stern et al., 1988; Bloomer et al., 1989a), occurs only in the northernmost NSP (north of Nikko) and the southern Volcano arc from Minami IwoJima to IwoJima (Bloomer et al., 1989a,b; Figure 2-2). The rest of the NSP, the northern Volcano arc lavas and most of the CIP belong to a subalkalic group, with both intermediate- and low-K suites showing the mineral assemblages of plagioclase-clinopyroxene-orthopyroxene-Fe-Ti oxides. Volcano size and K content do not seem well correlated. For example, lavas from the large island of Agrigan belong to a medium-K series, while the similarly large island of Nishinoshima has low-K lavas. There are seamounts with both intermediate and low-K samples.

Lavas from islands in the CIP define both slightly iron-enriched trends (Agrigan; Stern, 1979) and flat trends (Sarigan; Meijer and Reagan, 1981a) in total alkali-iron oxide-magnesia (AFM) plots. Most of the submarine edifices in the CIP, SSP, southern NSP, and northern Volcano arc fall within the same range in an AFM diagram as the CIP subaerial volcanoes, showing slight (Kita IwoJima) to moderate iron enrichment. Within the northern NSP and IwoJima region, only Minami IwoJima shows a distinct iron enrichment. Most of the other volcanoes plot near the lower part of the CIP field.

In the Izu-Bonin arc (Figure 2-3), the Bonin Ridge consists mainly of Paleogene high-magnesian andesite and boninite (27-40 Ma, Honza et al., 1981; Tsunakawa, 1983) and sedimentary rocks. The Shichito Ridge includes both subaerial and submarine edifices (Honza and Tamaki, 1985; Yamazaki et al., 1991). Volcanic rocks of the Shichito Ridge are divided into two groups in terms of alkalinity, i.e. low-alkali tholeiite (island arc tholeiite) in the northern part (Oshima to Sofugan islands) and high-alkali, tholeiite-alkaline rocks (shoshonitic affinity) in the southern part (Nishinoshima to Minami-IwoJima islands) (Yuasa and Tamaki, 1982; Stern et al., 1984; Yuasa, 1985; Stern et al., 1988; Bloomer et al., 1989b). Quaternary volcanic rocks from the Shichito Ridge (volcanic front) are known to be typical island arc tholeiite series and compositionally bimodal (Tsuya, 1937; Kuno, 1962; Philpotts et al., 1971; Ikeda and Yuasa, 1989). Felsic rocks are relatively abundant in the northern part of the Shichito Ridge, but sparse in the southern part (Yamazaki et al., 1991).

The volcanic rocks of IwoJima constitute a petrologically homogeneous group which Tsuya (1936) referred to as augite and augite-hornblende trachyandesites, distinctly more alkalic (9-10 wt % total alkalis) than the ordinary andesites (3-6 wt % total alkalis) of the Izu-Bonin-Mariana volcanoes or the average world andesite (Tsuya, 1937; Macdonald, 1948; Stern et al., 1984). Subaerial and submarine trachyandesitic lavas are chemically and isotopically very similar to the pumices erupted from IwoJima. Enriched magmas appear very early in the development of IwoJima and there are no examples from elsewhere in the Izu-Bonin-Mariana arc system where such LILE enriched andesites can be shown to be products of fractionation of arc tholeiitic basalts. The IwoJima Ridge was emergent and volcanically active in Middle Miocene time (16-10.5 Ma), but Early Miocene (22.5-16 Ma) sediments in the Shikoku basin are pelagic clays (Curtis and Echols, 1980) indicative perhaps that the IwoJima portion of the arc had not yet formed (Hawkins et al., 1984).

Notsu et al. (1983) claimed that the Sr isotopic compositions of different Izu-Bonin volcanic rocks from a single island are constant, and that the isotopic composition of the entire arc varies over a limited range ($^{87}Sr/^{86}Sr$ ranges between 0.7032 to 0.7038), as also substantiated in the data of Masuda et al. (1977), Nohda and Wasserburg (1981), Tatsumi et al. (1992), Yuasa and Nohara (1992) and Langmuir et al. (1994). The ε_{Nd} values of lavas from the northern part of the Izu-Bonin arc range slightly from +7.6 to +9.7 (Tatsumi et al., 1992; Langmuir et al., 1995). In addition, there are also some separate studies on REE (e.g., Masuda and Aoki, 1978; Fujimaki and Kurasawa, 1980; Lin et al., 1989; Yamamoto et al., 1992) and Sr/Ca-Ba/Ca systematics (e.g., Onuma et al., 1981, 1983) for Izu-Bonin volcanic rocks. There are a few datasets of combined major elements, trace elements and isotopes (Ikeda and Yuasa, 1989; Yuasa and Nohara, 1992; Tatsumi et al., 1992; Langmuir et al., 1995) for Izu-Bonin volcanic rocks, and these are used for comparing with the volcanic ash data of ODP Leg 125 in this thesis.

The Sr-Nd isotopic compositions of lavas from the Mariana arc and IwoJima region have been extensively reported (e.g., Meijer, 1976; DePaolo and Wasserburg, 1977; Stern, 1981,1982; Dixon and Stern 1983; Stern and Ito, 1983; Stern and Bibee, 1984; White and Patchett, 1984; Woodhead and Fraser, 1985; Woodhead, 1989; Lin et al., 1990; Stern et al., 1993). The $^{87}Sr/^{86}Sr$ ratios show a similar range to the Izu-Bonin arc from 0.70319 to 0.70392 whereas values of ε_{Nd} range from +2.4 to +9.5. There is a progressive decrease in ε_{Nd} along the Mariana-IwoJima arc from south (CIP, mean ε_{Nd} +7.0) to north (southern NSP, mean ε_{Nd} +5.3), and ε_{Nd} reaches a minimum (mean ε_{Nd} +3.6) at the northern NSP and IwoJima. ε_{Nd} values increase again to the north of IwoJima (mean ε_{Nd} +8.4). The mean Sr-isotopic composition increases in a complementary fashion from south (CIP, mean $^{87}Sr/^{86}Sr$ 0.70343) to north (southern NSP, mean $^{87}Sr/^{86}Sr$ 0.70362), reaching a maximum in the northern NSP and IwoJima (mean $^{87}Sr/^{86}Sr$ 0.70376). The Sr and Nd isotopic data fall broadly within the "mantle array " (DePaolo and Wassenberg, 1977) (or fan) but are displaced toward higher $^{87}Sr/^{86}Sr$ at a given ε_{Nd}.

For volcanic rocks from the Eocene through Miocene sections of the Philippine Sea plate, relatively few chemical data, particularly isotope and trace element data, exist. Very little work exists on the petrology and geochemistry of the Palau-Kyushu and West Mariana arcs. The most extensive petrologic and geochemical studies of Palau Kyushu igneous rocks were done by the International Working Group on the IGCP Project "Ophiolites" (1977) using suites of samples collected from dredge Sites 1396 and 1397 and by the Scientific party on the DSDP Leg 59 Site 448 (Kroenke, Scott, et al., 1980; Aldrich et al., 1980; Armstrong and Nixon, 1980; Ishii, 1980; Mattey et al., 1980; Scott, 1980). These rocks include vesicular subalkalic basalts and basaltic andesites. They contain common phenocrysts of labradioritic plagioclase, augite, bronzite and pigeonite with only rare pseudomorphic olivine. Chemically, they are typical of arc tholeiites with high FeO/MgO ratios and low Ba, Sr, Cr and Ni contents. Ingle, Karig, et al. (1975) drilled highly vesicular clasts typical of arc volcanism in volcaniclastic debris on the PKR at DSDP Leg 31 Site 296, some 1500 km north of DSDP Leg 59 Site 448 (Fig. 2-1); the petrographic character of this material is essentially identical to that encountered at Site 448. Volcanic rocks exposed on Guam, Saipan and Tinian, part of the forearc of the southern Mariana Ridge (Figure 2-2), are arc tholeiitic basalts, andesites, dacites, rhyolites and boninites of Late Eocene through Miocene age (e.g., Meijer, 1980, 1983; Reagan and Meijer, 1984).

However, no true lavas have been recorded from the West Mariana Ridge. The only drilled basement samples on the WMR (DSDP Leg 59 Site 451) are a few altered basaltic and basaltic andesitic breccias (Kroenke, Scott, et al., 1980). The petrological character of the WMR is based upon the petrography and abundances of relatively immobile elements of altered clasts within these breccias. Phenocryst assemblages in these highly vesicular clasts commonly contain plagioclase (andesine), augite, orthopyroxene and titanomagnetite (Ishii, 1980; Scott, 1983). The analysed samples from Site 451 on the WMR (Mattey et al., 1980) are highly altered and major element plots are not meaningful for purposes of classification. The high Al_2O_3 values and higher alkalic earth elements (AAE) contents (e.g., Ba 184 ppm, Sr 512 ppm) led Mattey et al. (1980) to term the WMR volcanics as a calc-alkalic series.

Most recently, Hickey-Vargas (1991) and Hickey-Vargas et al. (1995) studied the Sr, Nd and Pb isotopic variations in basin, oceanic plateau and island arc lavas from the pre-Miocene sections of the Philippine Sea plate using the well-documented samples cored on DSDP Legs 31, 58, 59 and 60. Lavas from Eocene-Miocene Philippine plate basins including the Daito, West Philippine, Parece Vela and Shikoku basins and Benham Rise have isotopic features of an Indian Ocean-type signature ((Hickey-Vargas et al., 1995). Modern Philippine plate basin lavas from the Mariana Trough and Sumisu Rift have isotopic characteristics consistent with their derivation from the same sources as the older basin lavas. However, lavas from the Eocene-Oligocene Palau-Kyushu Arc are clearly distinct from earlier and later basin lavas. Compared with the basin lavas, the arc lavas have higher $^{87}Sr/^{86}Sr$ for a given $^{143}Nd/^{144}Nd$ and systematically lower $^{208}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ for a given $^{206}Pb/^{204}Pb$ (Hickey-Vargas, 1991).

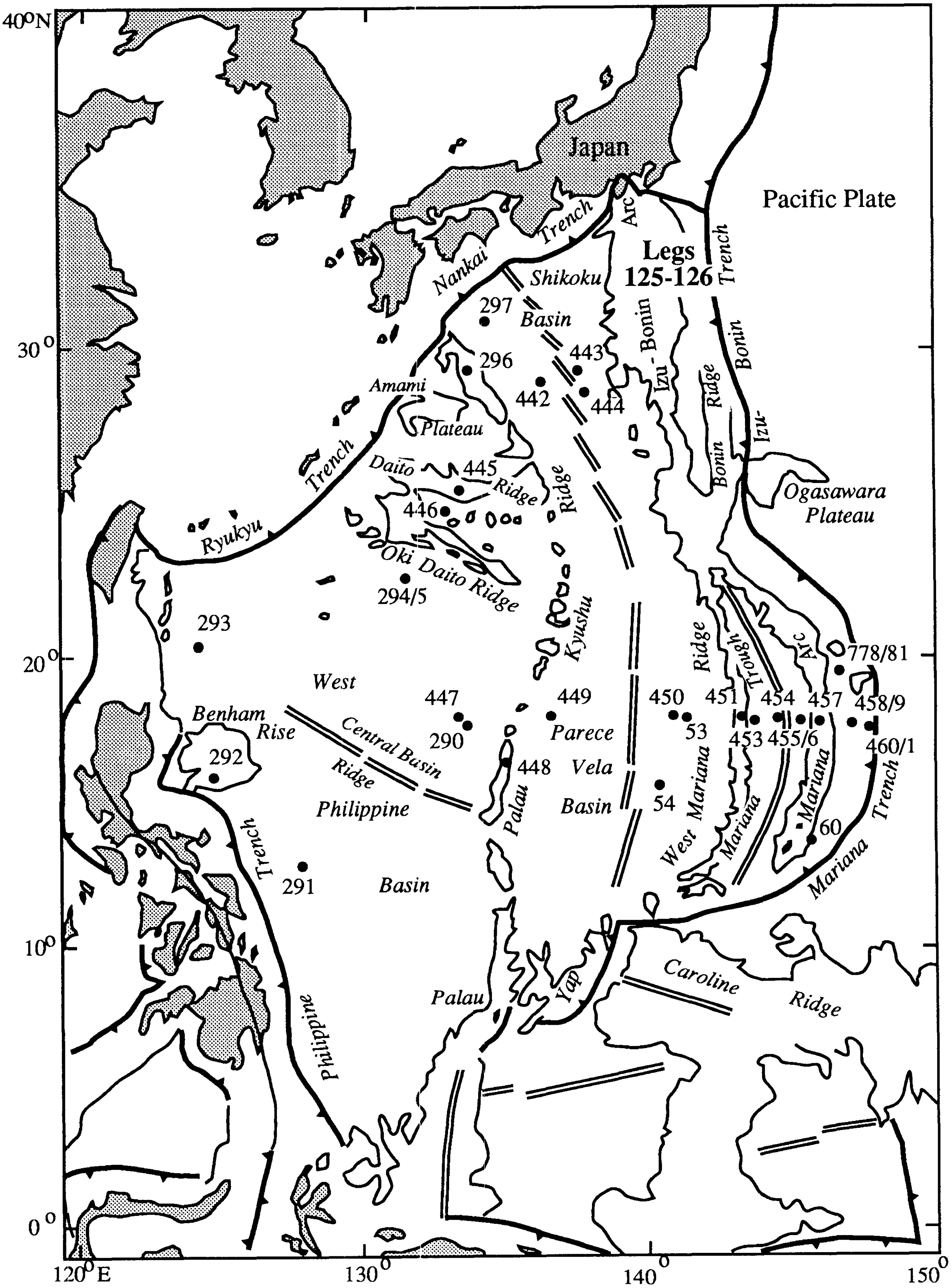

Figure 2-1 Location map for the Philippine Sea Plate and surounds, showing the location of ODP Legs 125 and 126 sites (see Fig 2-3 for details) in the Izu-Bonin-arc, and previous DSDP sites in the region. Barbed lines indicate subduction zones. Double lines indicate relict and active spreading centers. Basins and ridges are outlined by the 4-km bathymetric contour, except for the Izu-Bonin, West Mariana and Mariana arcs, which are outlined by a 3-km contour. Numbered filled circles are DSDP Legs 6, 31, 58, 59, and 60 sites. After Fryer, Pearce, Stokking et al. (1990a).

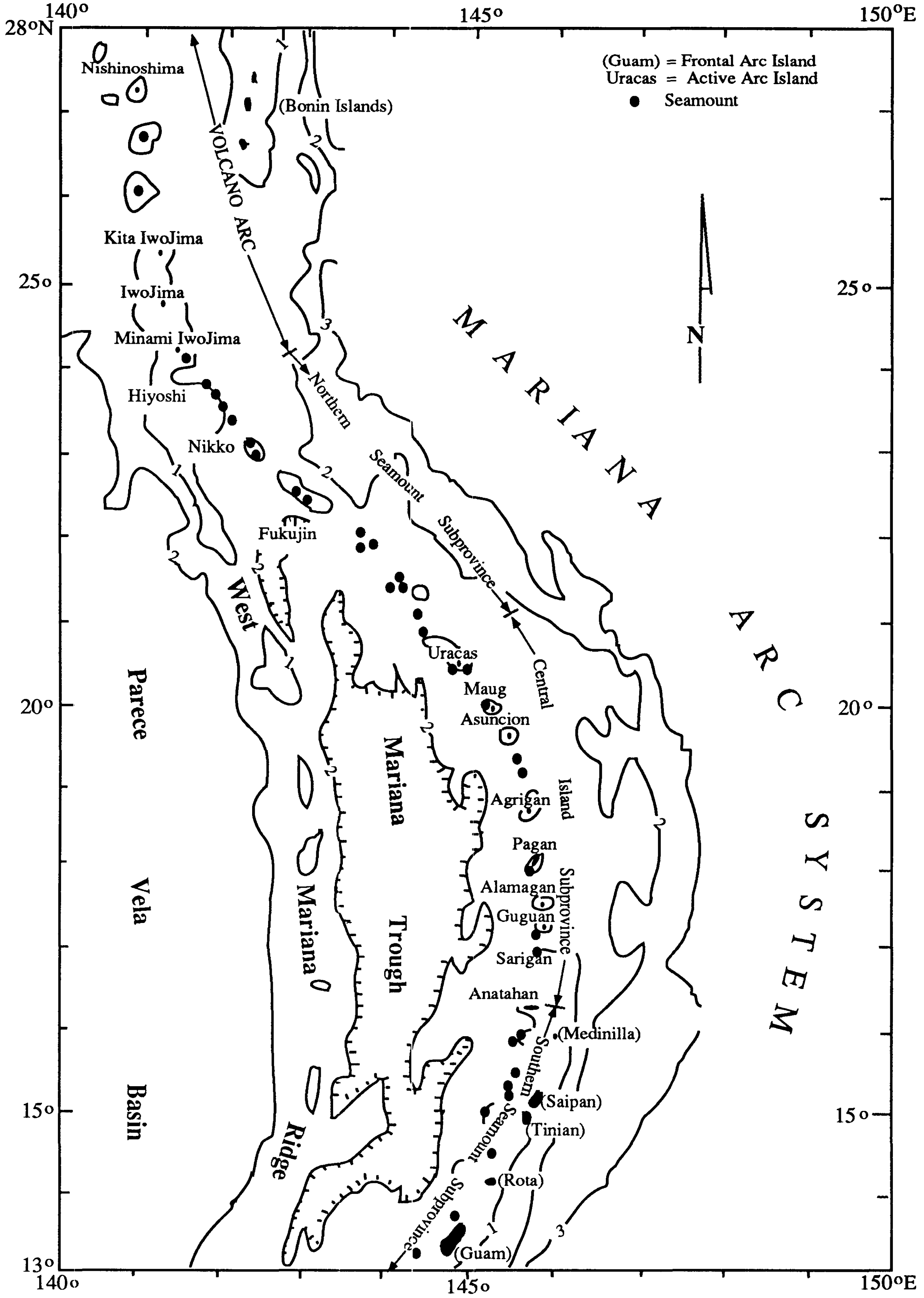

Figure 2-2 Location of major volcanic provinces in the Mariana Arc after Chase et al. (1968) and Bloomer et al. (1989). Depth contours are in kilometers.

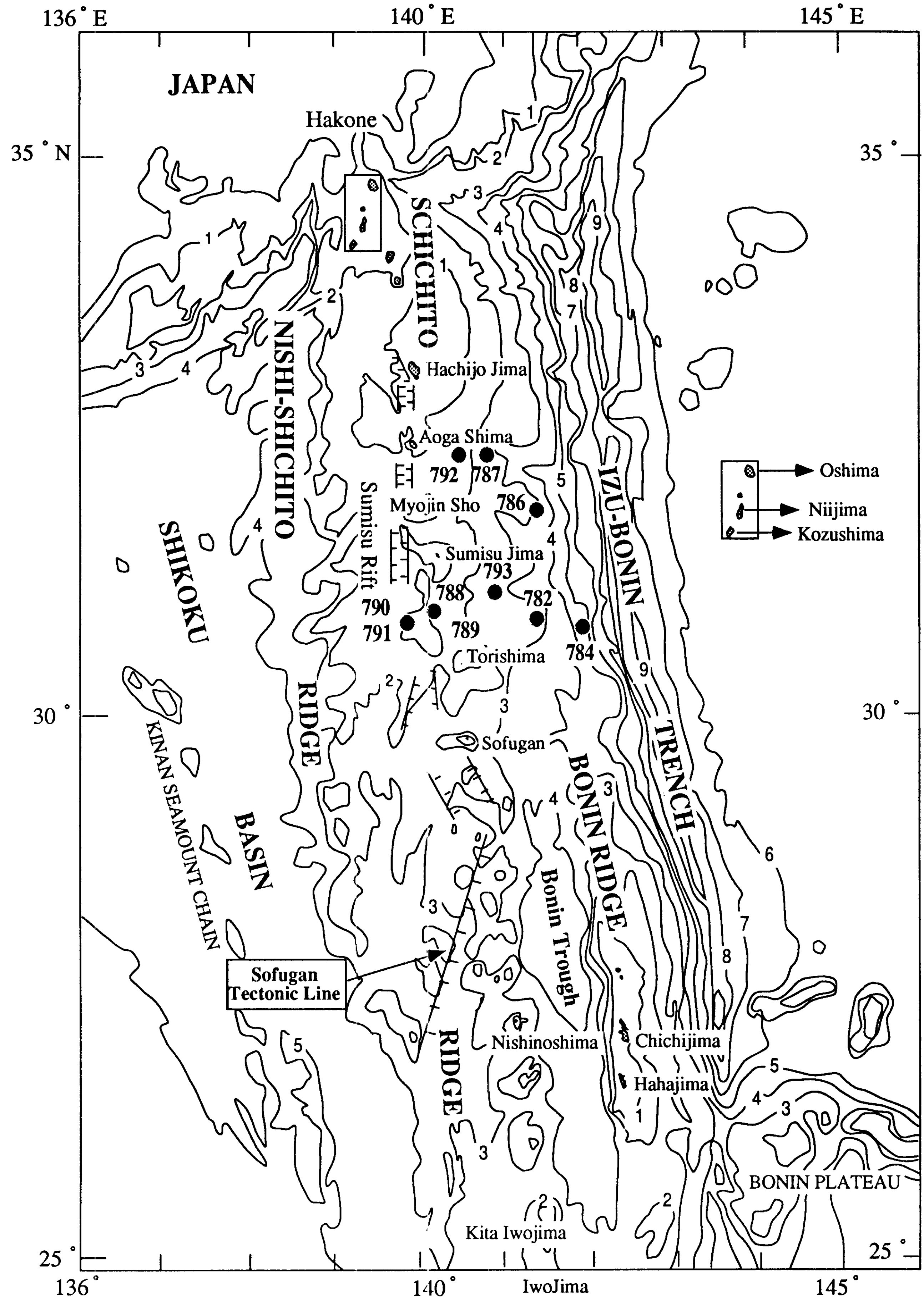

Figure 2-3 Location map of general Izu-Bonin arc-rift system and ODP Leg 125 Sites 782, 784, and 786, together with ODP Leg 126 Sites 787 to 792. Blathymetry and basement features are from Honza and Tamaki (1985), Ikeda and Yuasa (1989) and Arculus et al. (1992). Depth contours are in kilometers.

Chapter 3 Deep-Sea Volcanic Ashes: Samples from an Island Arc System

3.1 Introduction

Volcanogenic sediments result either primarily or secondarily from volcanic activity. These products can be pyroclastic, epiclastic. or authigenic in origin. Primary volcanic material consists of volcanic glass, crystals, and lithics, while secondary minerals include clay minerals derived from volcanic materials such as smectite and palygorskite and other minerals such as zeolites. Volcanogenic sediments are extremely important contributors to marine sediment accumulations (Lisitzin, 1972; Vallier and Kidd, 1977), particularly near island arcs where sedimentary wedges made largely of volcanic components can be several thousand meters thick. Even in areas greatly distant from volcanic centres, volcanogenic materials are of importance but are generally dispersed and masked by biogenic materials (e.g., Kennett, 1981). The marine geologic record contains three primary types of volcanic materials: pyroclastic material derived largely as ash falls from subaerial volcanoes; flows from submarine volcanoes; and submarine pyroclastic debris. Secondary epiclastic types also of importance are derived by reworking in the marine environment from preexisting pyroclastic deposits on land.

The air-fall deposits are commonly referred to as tephra. Tephra includes not only air-fall material but also pyroclastic flow materials such as ignimbrites - all pyroclastic materials derived from volcanoes. Tephra is a Greek word meaning ash, and it was placed into modern usage by Thorarinsson (1944). Aristotle (300 BC) had first used the term for volcanic ash derived from an active Italian volcano (Thorarinsson, 1974). In deep-sea sequences, we are concerned largely with air-fall volcanic materials - volcanic ashes.

3.2 Characteristics of deep sea volcanic ashes

The characterisation of volcanic ash and its relationship to eruption phenomena have been of interest to scientists since the time of Aristotle. Interest in this subject was renewed during mid-1800's when European naturalists began studying volcanic fields in the Mediterranean, South America, and Indonesia. With the invention of the scanning electron microscope (SEM), a full range of pyroclast sizes can be investigated and chemical changes on grain surfaces can be measured. Used in conjunction with optical microscopy and the electron microprobe, the SEM has allowed people to begin systematic characterisation of volcanic ash (Heiken and Wohletz, 1985). With development of microanalytical techniques, volcanic ash can be used to constrain the geochemical evolution of island arc systems (e.g., Arculus et al., 1995).

3.2.1 Definition of deep-sea volcanic ash

Classification schemes of volcanic ash are based upon grain size, composition of pyroclasts and magma, genesis of the pyroclasts, and mechanism of deposition. The most commonly used of these schemes is grain size, and is similar to that used in sedimentology to classify clastic sediments and sedimentary rocks. The classification recommended by the Subcommission on the Systematics of Igneous Rocks of the International Union of Geological Sciences (IUGS) is used here (Schmid, 1981; Fisher and Schmincke, 1984). Volcanic ash is any fragment, with a diameter ≤ 2 mm, ejected during an explosive volcanic eruption. The ash can be subdivided into two parts, coarse (≤ 2 mm in diameter) and fine (< 0.0625 mm in diameter). Deep-sea volcanic ash is any airborne fragment falling from an eruption cloud and resulting deposits preserved in deep-sea sediments.

The genetic classification of volcanic ash is based mainly on three categories suggested by Heiken (1972, 1974) and Heiken and Wohletz (1985). There are three basic mechanisms of volcanic ash formation: 1) explosive eruptions caused primarily by release of magmatic gases because of decompression within the magma as it reaches the surface of the planet (magmatic eruptions); 2) chilling and explosive fragmentation of magma during contact with ground and surface water or ice and snow (phreatomagmatic eruptions); and 3) the comminution and ejection of particles from vent walls or crater debris during eruptions of steam and hot water (phreatic eruptions). The shape and composition of volcanic ashes may be used to interpret physical properties of an erupting magma and its volatile content. These data may also indicate the degree of interaction between the magma and water or ice surrounding or overlying the volcanic conduit. Volcanic ashes produced by magmatic eruptions are predominant in the deep-sea sediments of the western Pacific arc system and are discussed in this thesis because they are most common and important.

3.2.2 Physical characteristics

Ash particles are like snow flakes in that no two are completely alike. They present an infinite variety of morphological, physical, and chemical characteristics (Heiken and Wohletz, 1985). Each ash grain can be regarded as a microscopic field area to be systematically mapped. On a statistical basis, the distinguishing characteristics of ash sample sets, consisting of thousands of grains, define general relationships that can be incorporated into the macroscopic world. Volcanic ash may consist of dense or inflated glass particles, crystals from the magma, solidified volcanic rocks of previous eruptions, or accidental fragments of country rock of any composition (lithics). Ashes are often highly distinctive, reflecting a single particular eruptive episode or episodes. Much work has gone into establishing various criteria in order to differentiate between ash layers and to identify the character of the eruptions that produced them, the possible sources of ashes and the mode of subsequent transportation (Kennett, 1981). Parameters that have been employed include: 1) physical characteristics of the ash layers themselves such as colour, thickness, and bedding characteristics, and of the individual shards such as size, shape, sorting, and internal structure such as bubbles; 2) mineralogical characteristics, which include mineral type and composition; and 3) geochemical characteristics, which include the major element and trace element features of individual glass shards and element and isotope characters of bulk ash layers.

The colour of ash layers is the most widely used criterion for distinguishing the layers from adjacent sediments. Colour contrasts have been used in conjunction with magnetostratigraphy for intercore correlations of ash layers (Ninkovich, 1968). The thickness of ash layers can provide important information. In general, the thicker the ash layers, the greater the eruptions (e.g. Kennett, 1981). Size classifications are also important. Fisher (1964) provided a classification based on size of volcanic products. Various studies have examined size changes with distance from the eruptive centre. One of the earliest well-documented studies was by Fisher (1964, 1965). He showed that in general, median diameter and sorting coefficients of tephra samples decrease with increasing distance from the source. As can be expected, a number of variables control the grain-size characters of an ash layer. These include viscosity and gas content of the magma and intensity of eruptions, which in turn control the size, shape, and density of fragments produced as well as their angle and weight of projection (e.g., Fisher, 1964, 1965).

A single ash layer may be composed of particles from single eruptive episode, or from several closely spaced eruptive episodes, or from contemporaneous eruptives from two or more separate sources. Abrupt changes in eruptive energy or wind variation during an eruption may produce bedding within a single layer. Sections closer to the eruptive centre often exhibit a coarser lower unit with a sharp top overlain by finer ashes. The lower, coarser unit results from an earlier plinian air-fall eruptive phase, while the fine upper unit results from fine-grained ash-fall deposits. In some cases, these two units have mixed together as shown by bimodal grain-size distributions in single ash layers (Sparks and Huang, 1980).

Morphology of shards is an important criterion used in studies on the genesis and composition of the volcanic ashes. Fisher (1963) differentiated volcanic glasses on the character of phenocrysts and the texture of the bubble wall in vesiculated glass. Heiken (1972, 1974) and Heiken and Wohletz (1985) clearly showed that the morphology of ashes is related to magma composition and eruption mode. Morphologic and petrologic characteristics of andesitic to rhyolitic ashes are related to higher viscosities and the higher volatile contents of their source magmas. These ashes represent some of the products of volcanism and most products of pelean and plinian eruptions. Andesitic ashes consist of complex mixtures of vitric, crystal, and lithic components. Vitric components include brownish to colourless, homogeneous to heterogeneous glasses. In equant to elongate pumice fragments, the particle shape depends on vesicle density and geometry. Many have parallel, highly elongate "pipe-like" vesicles that are parallel to the long axis of the pyroclast. There are no smooth particle surfaces and exposed broken vesicle walls provide sharp, irregular surfaces. Only the vesicle walls are smooth. Small particles, which are bits of vesicles wall, are Y-shape curved plates or simple needle-like forms. Phenocrysts broken out during explosive eruptions result in a crystal component in these ashes. Broken, angular mineral fragments are common; the particle shapes are governed by the fracture of the mineral. Most lithic fragments (a wide variety of rock types from vent and crater walls) are equant to elongate and angular to rounded. Surface textures are entirely dependent on the physical properties of the rock types.

Most dacitic and rhyolitic ashes are pumices or their broken products. Nearly all pumices are angular and highly vesicular. Narrow, elongate pumices usually contain highly elongate vesicles (with aspect ratios of more than 20 : 1) that are circular to lens-like in cross section and 5 to 50 µm in diameter. Pumice pyroclasts containing phenocrysts are generally heterogeneous. Some of the highly elongate varieties contain large, ovoid cavities around which thinner, elongate vesicles are bent. Large and less elongate pumices contain 100- to 500-µm long ovoid vesicles with aspect ratios of less than 20:1. Another pumice variety is massive with remarkably small vesicles (5 to 15 µm in diameter) and relatively thick (10- to 100-µm) vesicle walls. Many phenocrysts such as plagioclase and Fe-Ti oxides are coated with vesicular glass rinds. Vesicles are flattened ovoids that are paralleled or perpendicular to phenocryst surfaces and range from 80 to 300 µm long.

3.2.3 Mineralogical characteristics

A wide range of mineralogical criteria have been used to distinguish ash layers and to help infer the possible sources of ashes. These include mineral assemblage, mineral chemistry of feldspar, pyroxene and Fe-Ti oxides, and occurrence of other minerals such as quartz, amphibole, biotite, apatite, zircon and olivine. These minerals, when associated with glass in marine ash layers, are well sorted, highly angular, and fine-grained, suggesting dispersal by wind rather than by subaqueous transportation or by flotation (Kennett, 1981).

The mineralogical composition of individual ash layers is often very distinctive and homogeneous over large areas in the circum Pacific region (e.g., Kittleman, 1973). Carey and Sigurdsson (1978, 1980) have shown that variations in the crystal/glass ratio in the ash layers as a function of distance from the source can be a useful indicator of eolian differentiation. In ash layers from the Lesser Antilles arc, the denser phenocrysts are concentrated within 50 to 200 km from the source, whereas the more distant ash is predominantly composed of glass shards. These findings raise the possibility that the location of the source may be established by studies of crystal/glass fractionation patterns within an ash layer of unknown source.

In Tertiary sequences in the Philippine Sea, Donnelly (1975) observed that plagioclase is the most abundant constituent in all samples after glass. Zoning is common, reflecting either high viscosity or rapid cooling of the magma, both of which inhibit an early formed crystal from further reaction with the liquid phase. Coarser crystalline constituents, especially plagioclase and clinopyroxene, are characteristically shattered with concoidal fractures, reflecting highly explosive source eruptions. Orthopyroxene is relatively abundant in ashes representing large eruptions, while amphibole is more abundant in samples reflecting more limited volcanic activity. The orthopyroxene/amphibole ratio is probably useful in reflecting the relative intensity of eruptions (Donnelly, 1975). Coexisting clinopyroxene and orthopyroxene in relatively homogeneous ash layers can be used to calculate the possible equilibration temperatures of magmas (Arculus and Bloomfield, 1992).

Volcanic quartz is a relatively scarce mineral occurring generally with biotite, apatite, and to a lesser degree with alkali feldspar (Donnelly, 1975). Sanidine, a high-temperature alkali feldspar, is characteristic of some rapidly chilled volcanics. Alkali feldspar is of much more restricted occurrence in marine sediments. This mineral can be considered of primary volcanic rather than authigenic origin when the grains are fractured, lack inclusions, and are of generally fresh appearance. Authigenic potassium feldspar on the other hand is marked by euhedral crystals and abundant inclusions (e.g., Kennett, 1981). Fe-Ti oxides, when present, are particularly useful for the correlation of individual ash layers. Coexisting ilmenite and titanomagnetite pairs can be used to estimate the temperatures and oxygen fugacity (fO_2) of host magmas (e.g., Stormer and Whitney, 1985; Arculus et al., 1995). The concentrations of Ti, Cr, Zr, and V in Fe-Ti oxides have also been used by Lewis and Kohn (1973) to correlate marine ashes with those deposited on New Zealand.

3.2.4 Geochemical characteristics

Geochemical analysis of volcanic ash is becoming widely used as a distinguishing criterion and for information on magma composition and evolution (e.g., Kennett, 1981; Arculus and Bloomfield, 1992; Arculus et al., 1995). Analyses include the major elements and/or trace elements of bulk ashes (e.g. Borchardt et al., 1971; Bowles et al., 1973; Richardson and Ninkovich, 1976; Scheidegger et al., 1978, 1980; Ninkovich, 1979; Migdisov et al., 1980; Chen and Arculus, 1994a; Cao et al., 1995) and individual glass shards (e.g. Jones, 1973; Jezek, 1976; Scheidegger et al., 1978; Ninkovich, 1979; Packham and Williams, 1981; Pouclet et al., 1986; Arculus and Bloomfield, 1992; Fujioka et al., 1992a,b; Rodolfo et al., 1992; Cao et al., 1993; Lee and Stern, 1993; Chen and Arculus, 1993a, 1994b) and the Sr-Nd isotopic ratios of bulk glass or ashes (Egeberg et al., 1992; Chen and Arculus, 1993a,1994a; Cao et al., 1995).

For major and minor element studies on volcanic ash (glass), the simplest approach is indirect and involves the modal refractive index of glass shards (e.g., Ninkovich et al., 1964; Jones, 1973; Scheidegger et al., 1978; Kennett, 1981). This approach was a useful one for correlation and was widely applied until the 1980's (Kennett, 1981). More recently, electron microprobe analysis has become particularly important for major and minor element analysis of volcanic glasses because of its precision, efficiency, and its small sample requirements (e.g., Smith and Westgate, 1969; Jones, 1973; Scheidegger and Kulm, 1975; Jezek, 1976; Ninkovich, 1979; Packham and Williams, 1981; Arculus and Bloomfield, 1992, Arculus et al., 1995). The approach has proved of considerable value in the definition of the geochemical character of ashes, their correlation and any geochemical trends exhibited by the ash sequences through time.

For trace element analyses of volcanic ashes (glasses), however, there are limited data because of the existence of heterogeneous ash layers, the analytical techniques and the very small amounts of pure glass samples available. Most workers rely on the homogeneity of the volcanic ash layers and analyse the bulk ashes or glasses by wet chemical methods (e.g., Ninkovich, 1979), X-ray fluorescence (XRF) (e.g., Bowles et al., 1973; Richardson and Ninkovich, 1976), atomic absorption spectrophotometry (AAS) and instrumental neutron activation (INAA) methods (e.g., Borchardt et al., 1971; Scheidegger et al., 1980; Migdisov et al., 1980; Fujioka et al., 1986) and inductively coupled plasma source mass spectrometry (ICP-MS) (Chen and Arculus, 1994a; Cao et al., 1995). This assumption may be valid for some eruptions and some ash layers.

However, heterogeneous ash layers commonly exist (e.g., Jones, 1973; Jezek, 1976; Carey and Sigurdsson, 1978; Arculus and Bloomfield, 1992; Chen and Arculus, 1993a, 1994a,b). Jones (1973) identified single ash layers with two distinct compositions resulting from a mixed magma eruption. Jezek (1976) studied the compositional variations within and among volcanic ash layers in the Fiji Plateau area, southwest Pacific. He found that half of the ash layers have a SiO_2 range > 10 %, the compositional range is continuous in some layers, whereas in others a bimodal or polymodal distribution occurs. The wide range in major element compositions within individual ash layers from the western Pacific is also well-documented by Arculus and Bloomfield (1992) and Chen and Arculus (1994a,b). Analysis of individual glass shards is a more accurate measure of original lava composition than bulk ash analyses. Furthermore, the application of any method of trace element analysis must take this heterogeneity into account, and one should take great care to analyse homogeneous glass populations. Carefully examination by optical and electron microprobe should be taken before the bulk glass (ash) analyses are processed (Chen and Arculus, 1994b).

In contrast with the large amounts of major element data, and relatively limited trace element data on volcanic ash (glass), there are few Sr-Nd isotopic ratios (Egeberg et al., 1992; Chen and Arculus, 1993a, 1994a; Cao et al., 1995) and trace element data of individual glass shards (Arculus et al., 1992; Chen and Arculus, 1993a, 1994b; Clift and Dixon, 1994; Ewart and Griffin, 1994). Trace element analysis of ash sequences in cores from the eastern equatorial and southeast Pacific ocean has allowed identification and correlation of individual layers over wide areas (Bowles et al., 1973). Most recently, Egeberg et al.(1992), Arculus et al.(1992), Chen and Arculus (1993a, 1994a,b), Clift and Dixon (1994) and Cao et al. (1995) used the REE, LILE and HFSE patterns and Sr-Nd isotopic ratios to infer the possible sources of volcanic ashes recovered from the DSDP Leg 60 and ODP Legs 125, 126, 135 and 145. Correlations made within each area and possible sources inferred are based primarily on chemical and isotopic similarities intra- and inter- ash layers and nearby island arc volcanoes and on stratigraphic position. These studies conclude that all the volcanic ashes recovered on these specific legs were derived from destructive plate margins, i.e. island arc volcanism.

3.3 An approach to study of an island arc system

Most ash that is deposited as deep-sea sediment is derived from highly explosive volcanism associated with the active island arc and continental margin areas of the Earth. Island arc volcanism is marked by a large number of foci, the largest-scale eruptions and high explosive capacities. Magmas are highly viscous, and thus eruptions are typically highly explosive. Pyroclastic material makes up to 90 % of the solid products or even 99%, as in the Indonesian volcanoes (e.g., Kennett, 1981). Volcanism of low explosivity which is more typical of midocean and intracontinental volcanism contributes very little to deep-sea sediments except on a local scale. Lisitzin (1972) calculated that almost all of the total pyroclastic material produced since 1500 AD was produced in the island-arc and continental margin areas. As a result, most ash contributions are in the Pacific Ocean, the northeast Indian Ocean, the Gulf of Mexico and Caribbean, and in the Mediterranean Sea. This has been the case through most of the Cenozoic. However, Atlantic Cenozoic deep-sea sediments are largely devoid of ash layers except in the Iceland region and the Norwegian Sea (e.g. Kennett, 1981). Especially, most Cenozoic volcanic activity has occurred in the Circum-Pacific region and hence these areas are under the greatest influence of volcanic sedimentation.

Most volcanic eruptions eject tephra to a height of less than 6 km (Lisitzin, 1972), and the ash is thus only locally distributed. More rarely, ash is ejected into the stratosphere at heights greater than 10 to 15 km. As a result, the ash is transported 3000 to 6000 km from volcanic centres (Eaton, 1963). Very fine material (0.3 to 1 μm) may be distributed over vast areas on a meridional basis. These might be termed global ash falls (Kennett, 1981).

3.3.1 Advantage of deep-sea volcanic ash studies

1. Deep-sea sedimentary sequences are generally simpler to interpret than those deposited on land because of the availability of continuous or near-continuous sections and general abundance of fossils. Hence the stratigraphic relations among different ash layers are readily determined. Furthermore, single volcanic ash layers can be traced over distances as great as 4000 km, which cannot readily be accomplished on land. Thus much of the information which can be derived from ashes requires extensions of land-based studies in the marine realm, where within 1000 km of the source, ashes may be found as clear and megascopically distinguishable layers

(Watkins and Huang, 1977). Nevertheless, fine volcanic glass particles, representing either distant sources or less violent eruptions, are common in many deep-sea sediments without being readily distinguishable from the background sediment.

2. The availability of magnetostratigraphy and biostratigraphy can provide a firm chronological basis for ash layer sequences (e.g., Self and Sparks, 1981). Therefore, ash layers provide isochronous and often readily traceable levels for intercore correlations (e.g. Kennett, 1981).

3. Deep-sea tephra deposits provide important information on individual explosions or series of volcanic explosions. The intensity of eruptions, volumes of material produced, and perhaps even the eruptive duration can now be estimated within certain limits.

4. Volcanic ash layers provide valuable information on the petrochemistry of volcanic sources and changes in the geochemical character of a source region through time (e.g., Scheidegger and Kulm, 1975; Arculus et al., 1995).

5. Sequences of volcanic ash layers provide critical information about the tectonic history of source regions. Attempts have been made to relate the history of volcanism to local or regional tectonics of source regions. Episodicity of volcanism has been observed in volcanic sequences, and the timing of volcanic activity may have occurred over large areas throughout the Cenozoic irrespective of local setting (McBirney, 1971; McBirney et al., 1974; Kennett and Thunell, 1975; Kennett et al., 1977; Cambray and Cadet, 1994). The beginnings of volcanism are also important in heralding the beginnings of active tectonism in particular regions such as the Izu-Bonin-Mariana arc-backarc region (e.g., Taylor, 1992).

6. Deep-sea tephras provide the best available sequences for studying temporal relations between paleoclimatic and volcanic history (e.g., Kennett and Huddlestun, 1972b).

7. Valuable information can be provided on the wind patterns or other transportation and depositional histories (e.g., Eaton, 1963; Cambray et al., 1993).

8. Because ash layers represent essentially instantaneous geologic events, the stratigraphic distribution of ash particles from individual layers is a useful criterion for determining the degree of reworking of sediments by burrowing organisms.

3.3.2 Disadvantage of deep-sea volcanic ash studies

However, there are some problems with studies of deep-sea volcanic ash as simply addressed by Gill et al. (1994) and Arculus et al. (1995): 1) considerable information can be lost through drilling (rotating coring) disturbances which often effectively destroys thin ash layers in less coherent sediments; 2) the percentage of the ash sections recovered may only be high when advanced piston coring is carried out with core overlap; 3) susceptibility to alteration and problems of digenetic change as a result of exposure to sea water may prevent use of older volcanic ash beds for geochemical study; 4) it is difficult to precisely identify the sources of deep-sea volcanic ashes due to their airfall and the possibility of multiple and simultaneous eruptions; 5) typically, the volcanic ash layers are thin, < 1-2 cm thick, and heterogeneous (e.g., Jezek, 1976; Huang, 1980; Arculus and Bloomfield, 1992), which may limit comprehensive trace element and isotopic analysis; 6) the majority of deep-sea volcanic ashes are chemically andesitic to rhyolitic, corresponding to intermediate to felsic explosive eruptions.

3.3.3 Review of volcanic ash studies

Volcanic ash studies were first carried out on readily accessible on-land sequences. With the advent of suitable coring techniques for deep-sea sediments in the 1950's, there has been increasing focus on marine ash layers which often provides sequences simpler to interpret. For many years, initial ash studies on land and in the marine environment concentrated largely on ash layers simply as correlation tools (see Kennett, 1981 for a review). During the 1960's, the first detailed ash studies which included mineralogical and grain-size data were begun on megascopically distinct layers (e.g., Ninkovich et al., 1964). Ninkovich et al. (1964) traced ash layers over a distance of 400 miles from their source in the South Sandwich Islands and correlated them using the mineralogy and the refractive indices of the glass. Detailed dating of ash layers by magnetostratigraphy provided an important chronological basis for study of the volcanism that created the ash layers (e.g., Ninkovich et al., 1966). The first application of the use of geochemical analyses in the identification and correlation of ash layers was made by Bowles et al. (1973). Up until the early 1970's, all studies had examined only the megascopically distinct ash layers in deep-sea sediments and restricted studies to the sand-sized and larger fractions (> 0.062 mm). In 1975, Huang et al. developed a system of separating, counting, and size analysing dispersed volcanic glass as fine as 0.011 mm in deep-sea sediments. The possible relationship between the volcanic ash record in deep-sea sediment sequences and paleoclimatic record was first examined by Kennett and Huddlestun (1972a,b).

With the development of the Deep Sea Drilling Project (DSDP) in 1968 and the successor Ocean Drilling Program (ODP) in 1985, volcanic ash studies have made great progress. Basic data on ash layer distributions have been published in the DSDP Initial Reports since 1968. Compilations of DSDP reports were attempted by Kennett and Thunell (1975), in a study of late Cenozoic ash layer distributions. The importance of these and later studies (e.g., Kennett and Thunell, 1975; Scheidegger and Kulm, 1975; Kennett et al., 1977; Hein et al., 1978; Scheidegger et al., 1978; Paterne et al., 1990; Pubellier et al., 1991; Cambray et al., 1993; Cambray and Cadet, 1994) is the demonstration of episodicity in volcanism within regions and perhaps on an oceanwide basis, thus providing critical information on the nature of volcanism itself. Furthermore, Scheidegger and Kulm (1975) were the first workers to demonstrate possible geochemical cyclicity in marine ash sequences, an observation fundamental to the understanding of the genesis of the volcanism. Generally, the majority of volcanic ash studies are limited to: 1. the general description and distribution of ash particles and ash layers; 2. major and minor element analysis of glass and mineral by EMP; 3. discussion of glass alteration, volatile (difference between 100 and total major and minor oxides by EMP); 4. rock series (tholeiitic, calc-alkali and alkaline) by K_2O+Na_2O wt% (Kuno, 1960, 1966), K_2O vs. SiO_2 wt% (Gill, 1981), FeO*/MgO ratio (Miyashiro, 1974) and AFM (Irvine and Baragar, 1971); 5. correlation among drilled cores between land and marine environments by the similarities of physical and chemical characteristics of ash layers and similar ages; and 6. possible sources inferred from the similarities between the features of volcanic ash (glass- only or including mineral + lithic fragment) and nearby island arc volcanic rocks. In contrast, few volcanic ash studies have involved analyses of heterogeneous ash layers (Arculus et al., 1992; Chen and Arculus, 1993a,1994b) and the geochemical evolution of island arc systems (Chen and Arculus, 1994a; Arculus et al, 1995) due to the limited data availability.

3.4 The volcanic ash perspective on the IBM arc system

Studies of volcanic ashes of the Izu-Bonin-Mariana arc system have depended largely on the results of the DSDP Legs 6, 31, 58, 59, 60 (Fischer, Heezen, et al., 1971; Karig, Ingle, et al., 1975; Klein, Kobayashi, et al., 1980; Kroenke, Scott, et al., 1980; Hussong and Uyeda, 1981) and ODP Legs 125 and 126 (Fryer, Pearce, Stokking, et al., 1990a, 1992; Taylor, Fujioka, et al., 1990, 1992) on the Philippine Sea plate, because virtually the entire area is submerged, and the islands are so small that it is difficult to correlate marine tephras to their land sources (e.g., Machida and Arai, 1983, 1988; Furuta et al., 1986). The geology and geophysics of the Izu-Bonin and Mariana arcs were summarised by Karig and Moore (1975a,b) from the results of DSDP Leg 31. More recently, Honza and Tamaki (1985) and Yuasa and Murakami (1985) compiled the geological and geophysical data of the Izu-Bonin arc and Tatsumi et al. (1992), Yuasa and Nohara (1992) and Langmuir et al. (1995) have discussed in detail the geology and geochemistry of the Izu-Bonin arc area. Woodhead (1988. 1989), Bloomer et al. (1989a,b), Lin et al. (1989, 1990), Stern et al. (1988, 1989, 1993) and Hickey-Vargas (1991) have summarised the geology and geochemistry of the Mariana arc region. From marine geophysical studies, together with drilling studies of DSDP Legs 6, 31, 58-60 and ODP Leg 125 and 126, volcanism in the Philippine Sea plate has been placed in the context of the opening of the Sumisu Rift and Mariana Trough, the Shikoku and Parece Vela basins and marginal seas (e.g., Kobayashi and Nakada, 1979; Seno and Maruyama, 1984; Taylor, 1992). Therefore the temporally well-constrained tectonics and geology of the IBM arc-backarc system coupled with the large amount of geochemical data available for this system provide an excellent opportunity to study the geochemical evolution of a suprasubduction zone environment through analysis of the nearby marine volcanic ashes.

Marine ash studies of the Izu-Bonin arc have lagged behind those of the Mariana arc region because DSDP Legs 6, 31, 58, 59, and 60 were drilled before ODP Legs 125 and 126. In the 1970's and early 1980's, ash studies concentrated largely on the general description of layers (colour, size, thickness and components), distribution and ages of layers, and relationship between layers and arc volcanism and backarc spreading (Fischer, Heezen, et al., 1971; Karig, Ingle, et al., 1975; Klein, Kobayashi, et al., 1980; Kroenke, Scott, et al., 1980; Hussong and Uyeda, 1981). Limited data were published on the major and minor element chemistry of glasses from Leg 60 Sites 453 and 454 (Packham and Williams, 1981) and the trace element chemistry of bulk vitric tuff from Leg 59 Sites 448 and 451 (Migdisov et al., 1980). In 1987, Warner et al. studied the major and minor element chemistry of glasses and minerals from Leg 59 Site 450. Most recently, the volcanic ashes recovered from DSDP Legs 6, 31, 58-60 drilled on the Philippine Sea plate have been extensively studied by many workers using major and minor element of glasses (Lee and Stern, 1993; Straub, 1993) and using major, minor, and trace element of individual glass shards and trace element and Sr-Nd isotopic ratios of bulk ashes (Arculus et al., 1992; Chen and Arculus, 1993a, 1994a,b). These ash studies show that the marine volcanic ashes recovered from DSDP Sites drilled in the Mariana Trough are all from volcanic activity on the present Mariana active arc. Ashes of Sites 449 and 450 in the Parece Vela basin are from the WMR remnant arc, and ashes of Sites 290 and 447 in the West Philippine Basin are from the PKR remnant arc. The ashes of Sites 458 and 459 in the present Mariana forearc record all the volcanism of the active Mariana ridge from ~ 5 Ma to the present, the West Mariana Ridge from ~ 22 to 6 Ma, and the Palau Kyushu Ridge from ~ 35 to 23 Ma. The overwhelming majority of thousands of analysed glass shards are tholeiitic based on AFM (Irvine and Baragar, 1971) and Miyashiro's (1974) discriminants and low-K to medium-K series based on the classification of Gill (1981). Compositions range from basalt through andesite to dacite and rhyolite.

Arculus and Bloomfield (1992), Arculus et al. (1992), and Chen and Arculus (1993a; 1994a,b) made detailed major element, trace element and Sr-Nd isotope geochemistry studies of volcanic ashes recovered from ODP Leg 125 Sites 782, 784 and 786 drilled in the Izu-Bonin forearc (see Figures 2-1 and 2-3). The total age range of the ash layers is from Eocene to Pleistocene (Fryer, Pearce, Stokking, et al., 1990a), although not all sites cover this full span. There were two periods of greatest intensity, one from the Late Miocene to the present day (~ 5-0 Ma) and one during the Eocene-Oligocene (about 45-30 Ma) (Leg 125 shipboard scientific party, 1989). The composition of glass ranges from basalt through andesite and dacite to rhyolite, and generally belong to a tholeiitic, low-K suite. There is no indication of any regular secular change during the evolution of the Izu-Bonin arc from tholeiitic through calc-alkalic to alkaline compositions with time (Arculus and Bloomfield, 1992; Chen and Arculus, 1993a; 1994a). In Sites 782 and 784, rare high-K rhyolite compositions of Late Miocene and Pleistocene age are present, indicating that they may derive from the cross-arc chains (e.g., Kozushima) in the northern Izu portion, or from the alkali-rich sequences erupted at the Minami-IwoJima / IwoJima volcanoes at the junction between the Izu-Bonin and Mariana arcs (Arculus et al., 1992; Chen and Arculus, 1993a).

Fujioka et al. (1992a,b) studied volcanic ash recovered from ODP Leg 126 Sites 787-793 drilled on the Izu-Bonin forearc and volcanic front, and in the active backarc Sumisu Rift. White and black tephra layers (393 in number) were deposited from the Oligocene to the present. The tephra frequency increased in the Late Eocene to Early Oligocene and the Pliocene-Pleistocene, with a small increase in the Middle Miocene (about 10 Ma). Quaternary tephras, with variable proportions of basaltic and rhyolitic compositions, increase in frequency at around 0.6 and 0.3 Ma. The chemistry of the tephras from the Izu-Bonin forearc is notably bimodal (basaltic and rhyolitic) since the Late Pliocene, which suggests that the predominant stress field over that period has been tensional, as in the Cascade region of western North America. The pumices from the backarc Sumisu Rift are all low-K rhyolites. Most of the tephras belong to the low-alkali tholeiitic series of Kuno (1960, 1966) and the low-K series of Gill (1981). High-K series tephras occurred from 3 Ma to the Holocene, some of which may have been derived from the Ryukyu arc and other sources far to the west. The ash study of the Izu-Bonin arc-backarc region (ODP Leg 126 Sites 788-791) by Rodolfo et al. (1992) and Nishimura et al. (1992) yielded a similar conclusion.

Egeberg et al. (1992) studied the trace elements and Sr-Nd isotopic ratios of glass shards from 26 megascopic tephras of Site 792 drilled in the Izu-Bonin forearc. The distribution of $^{87}Sr/^{86}Sr$ (group I: 20/26, 0.70326-0.70404, group II: 6/26, 0.70373-0.70510) and $^{143}Nd/^{144}Nd$ (group I: 0.51300-0.51311, ε_{Nd} 7.1-9.2; group II; 0.51248-0.51281, ε_{Nd} -3 to +3) isotopic ratios indicate that the glass separates contain less than 10 % of palagonitized glass or secondary alteration minerals. Correlation diagrams and multivariate analyses identify four tholeiitic groups, two calc-alkalic groups, and one group with glass of shoshonitic affinity. The tholeiitic ash layers were derived from volcanoes on the Izu-Bonin arc, most probably from the volcanic island Hachijojima. The calc-alkalic ashes and ashes with shoshonitic affinity were probably derived from volcanism along the Ryukyu arc. However, Egeberg et al. (1992) did not analyse the major elements of these glass separates. From their INAA data of Na and Ti , these glass separates are probably rhyolites. The published REE patterns are of poor quality or glass separates are possibly mixtures of glass with minerals or sediments.

3.5 Test of validity of volcanic ash studies

As outlined above and in the Appendices, the unique geological and tectonic setting of the IBM arc-backarc system, the extensive on-land studies of IBM volcanic rocks, the availability of a complete set of volcanic ash samples spanning the arcs' explosive history from about 42 Ma to present, coupled with the advanced analytical techniques available for heterogeneous and small ash samples, provide an excellent opportunity to test the validity of volcanic ash studies. In this thesis, I make use of the advantages of ash occurrences and attempt to overcome their disadvantages. I attempt to answer some questions about the IBM arc system addressed in Chapter 1. Studies of marine volcanic ashes near the IBM arc-trench system will contribute to our knowledge of the tectonic history of the western Pacific and the origin of magmatism in arc-backarc basin systems.