Chapter 6 Trace Element Characteristics of Individual Glass Shards from DSDP Leg 60 and ODP Leg 125 Ash Layers

6.1 Introduction

The occurrence of compositionally heterogeneous volcanic ash layers has been recognised for a long time (e.g., Jezek, 1976; Arculus and Bloomfield, 1992). Workers have used only the electron microprobe to study these heterogeneous volcanic ashes or used INAA, XRF or ICP-MS to study the bulk ashes (assumed homogeneous ashes) (see Chapter 3 for a review). Published trace element data of individual glass shards from island arc volcanism are currently few. Arculus et al. (1992) and Chen and Arculus (1993a, 1994b) reported briefly some trace element data of individual glass shards from the Izu-Bonin-Mariana volcanic ashes. This Chapter will present in some detail the trace element geochemistry of individual glass shards.

On the basis of ~ 1750 sets of major element analytical data of individual glass shards from ~ 185 bulk ash samples, 220 individual glass shards (125 from DSDP Leg 60 and 95 from ODP Leg 125) were chosen for further studies of selected trace element (Rb, Ba, Sr, Zr, Y, Cu, Zn and Ga) abundances using the Heavy Ion Analytical Facility (HIAF) Proton Microprobe (PMP) at the CSIRO, Sydney. These selected individual glass shards span the arcs' explosive history from ~ 42 Ma to present, cover the whole range of rock types from basalt through andesite and dacite to rhyolite (Figure 6-1A), and also include low-K to medium-K to high-K tholeiitic series (Figures 6-2A,C). Therefore, these 220 individual glass shards are geochemically representative of the Izu-Bonin and Mariana arc volcanic glasses. The classification and nomenclature for glass types and rock series are taken from Chapter 4.

6.2 Trace Elements of Glass shards from Leg 60 and Leg 125 ash layers

The trace element abundances of all 220 individual glass shards determined by PIXE-PMP, combined with major element data measured by EMP-EDS, are given in Appendix 3.3, and plotted against age in Figures 6-1A,B. Overall during the development of the IBM arc system, the major and trace element abundances have a restricted range but large ion lithophile (LIL) elements such as K, Rb, Ba, and Sr have peaks at ~ 20 Ma, 8-11 Ma, and ~ 2 Ma in the Marianas, similar to the high-K pulses described earlier. Additionally, there are peaks in Cu abundance in the IB arc at ~ 7 Ma and 13 Ma. The element ratios such as K/Rb, K/Ba, K/Sr, Ba/Rb, Ti/Zr, Rb/Sr, Zr/Y, and Sr/Y also have a restricted range. As discussed in Chapter 4, the IBM glasses can subdivided into three subgroups: L125 Gl, a predominantly low-K series of 0-17 Ma age; L60A Gl, a predominantly low-K series of 18-35 Ma age; L60B Gl, a predominantly medium-K series of 0-17 Ma age, based on the K_2O-SiO_2 classification diagram (Gill, 1981). The acquired 220 element data are plotted against SiO_2 in the form of time intervals (L125 Gl 0-17 Ma, L60A Gl 18-35 Ma, and L60B Gl 0-17 Ma) in Figures 6-2A,B.

The chemical compositions of the three subgroups of glasses form a tight continuum from basalt, basaltic andesite through andesite to dacite and rhyolite (Figures 6-2A,B). Generally, L125 glasses are very similar to L60A glasses in every aspect (major and PMP trace element compositions), but are significantly different from L60B glasses in K_2O, CaO, Rb, Ba, Sr abundances and CaO/K_2O ratio at a given SiO_2. The majority of L60B andesitic glasses have higher K_2O (0.5-2.0%), Rb (10-45 ppm), Ba (250-800 ppm), and Sr (250-600 ppm), similar TiO_2 (0.7-1.5%), Zr (40-110 ppm), Y (20-40 ppm), Ga (8-20 ppm), Cu (10-250 ppm) and Zn (70-160 ppm), but lower CaO (9-5%) and CaO/K_2O (15-3) relative to those of the majority of L60A and L125 andesitic glasses (K_2O < 0.5%, Rb < 18 ppm, Ba 20-250 ppm, Sr 100-250 ppm, TiO_2 0.7-1.5%, Zr 30-90 ppm, Y 15-35 ppm, Ga 8-20 ppm, Cu 10-250 ppm, Zn 70-160 ppm, CaO 11-7% and CaO/K_2O 40-15). Interestingly, L125-L60A group and L60B group glasses have very similar ranges of LIL element ratios such as K/Rb 200-1000, K/Ba 10-40, K/Sr 10-40, Ba/Rb 15-50, and Rb/Sr 0.02-0.10, but different HFS element ratio ranges with the latter having lower Ti/Zr (100-50) and higher Zr/Y (2.5-4) relative to the former with Ti/Zr (200-100) and lower Zr/Y (1-2.5) in the andesite range.

6.3 Trace element comparison of volcanic glasses and IBM volcanic rocks

There have been extensive separate and combined studies of the Izu-Bonin and Mariana arc-backarc system, as briefly described above. References for the data collected for the IBM arc-backarc system are listed in Chapter 4. Relative to the major element data, there are fewer combined major and trace element data sets. Of the more readily available trace elements, representative LILE (K, Rb, Ba, and Sr) and HFSE (Ti, Zr, Y) have been selected to compare arc-backarc magma compositions. Variations in the ratios of the moderately incompatiable HFSE are particularly useful for assessing the intrinsic fertility of the mantle wedge without slab input (Arculus et al., 1991; Pearce and Parkinson, 1993).

Selected trace element data of the three ash subgroups and the IBM arc, backarc volcanic rocks and MORB are first plotted in a diagram of Y vs. Zr (ppm) (Figure 6-3). The three subgroups of glasses show some overlap. In detail, L60A glasses and L60 LM glasses (Late-Middle Miocene Leg 60 glasses) overlap the main trend of the Eocene-Oligocene Mariana arc volcanic rocks (Site 448 basement and Guam-Saipan volcanic rocks) and Late-Middle Miocene Mariana arc volcanic rocks (Site 451 basement and Guam-Saipan Miocene volcanic rocks), respectively. There are some scatter points on the Y vs. Zr diagram, which may be due to analytical problems with older volcanic rocks. There is also overlap of the modern Mariana volcanic rocks with the younger group of Leg 60 glasses (L60 QP), but at higher Zr/Y than the older glasses. The Izu-Bonin subaerial and submarine volcanic rocks with the exception of IwoJima are identical to the Leg 125 glasses, and similar to the older Mariana glasses. IwoJima has the highest Zr contents (180-270 ppm), intermediate Y abundances (30-45 ppm) and consequently the highest Zr/Y. Interestingly, the IBM backarc basin volcanic rocks except the Daito Basin volcanic rocks and half of the West Philippine Basin volcanic rocks have the same trend on the Y-Zr diagram with MORB and the IBM glasses. The abundances of Zr and Y for the representative MORB and backarc basin volcanic rocks concentrate in the ranges 40-180 ppm and 15-60 ppm, respectively, while those for IBM glasses are 30-160 ppm and 10-50 ppm, respectively. The Daito Basin volcanic rocks have much high Zr contents (130-300 ppm) but similar Y abundances (15-40 ppm). However, the West Philippine Basin volcanic rocks have the lowest Zr contents (only 35-70 ppm) at similar Y abundances (20-40 ppm).

Comparison of the abundances of six selected elements (Rb, Ba, Sr, Ti, Zr, and Y) and their element ratios against SiO_2 (wt %) for Mariana glasses and Mariana arc volcanic rocks are shown in Figures 6-4A,B and C. The Quaternary-Pliocene glasses (L60 QP) are similar to modern Mariana arc volcanic rocks in Ba, Rb, Zr, and Y but have higher TiO_2 (0.8-1.5 wt%) and lower Sr (200-350 ppm) in the andesite range relative to the volcanic rocks, possibly due to plagioclase accumulation in the latter. The Late-Middle Miocene glasses are similar to the contemporaneous arc volcanic rocks in Rb, Ba, Zr, Y, and TiO_2 but have general lower Sr abundances (200-500 ppm) relative to the rocks (400-1000 ppm). The Oligocene glasses are compositionally similar to the Eocene-Oligocene arc volcanic rocks but with more scatter in abundances. The broadly positive relationship between Rb, Ba, Zr, Y and SiO_2, and generally negative correlation between TiO_2 and SiO_2 support the conclusion inferred from major element studies that the genesis of the spectrum of glass compositions was dominated by fractional crystallisation.

Generally, the element ratios of K/Rb, K/Ba, Ba/Rb and Zr/Y of Mariana LM-QP glasses are in the same range of the Mariana LM-QP arc volcanic rocks. However, the same ratios of Pre-Miocene Mariana arc volcanic rocks are much more scattered with about half of the Site 448 basement volcanic rocks having high K/Ba (> 100-400) and low Ba/Rb (2-10), a result of relatively low Ba abundances. There is overlap of element ratios of K/Rb, K/Ba, Ba/Rb, and Zr/Y of L60A glasses and Eocene-Oligocene Mariana arc volcanic rocks. Interestingly, there are broadly positive correlations between K/Sr or Rb/Sr vs. SiO_2 for these Mariana glasses and volcanic rocks except for a subset of Site 448 basement volcanic rocks which are characterised by large ranges of K/Sr and Rb/Sr ratios at a given SiO_2. The Sr/Y ratios of Eocene-Oligocene volcanic rocks are generally lower than those of the glasses but the Sr/Y ratios of Miocene-present volcanic rocks are higher than those of glasses of the same age range. There is broadly negative correlation between the Ti/Zr and SiO_2 for all Mariana glasses and volcanic rocks. Some of the basalts and basaltic glasses have higher Ti/Zr values (100-200).

The comprehensive comparisons of six representative elements Rb, Ba, Sr, Ti, Zr, Y and their element ratios vs. SiO_2 (wt %) for Izu-Bonin glasses and Izu-Bonin arc volcanic rocks are shown in Figures 6-5A,B and C. The Izu-Bonin glasses have very similar composition with Izu-Bonin arc volcanic rocks (subaerial and submarine) except IwoJima volcanic rocks in Ba, Rb, Sr, Y, K/Ba, K/Rb, K/Sr, Ba/Rb, Sr/Y and Rb/Sr but have high TiO_2 (0.8-1.5 wt%), high Ti/Zr (120-220 ppm), low Zr (20-60 ppm) and low Zr/Y (1.5-2.5) at the andesite range relative to the volcanic rocks. The IwoJima volcanic rocks have much higher Rb (55-100 ppm), Ba (1000-2000 ppm), Sr (400-800 ppm), Zr (180-270 ppm), Zr/Y (5-9), K/Sr (40-100), Sr/Y (15-25), and Rb/Sr (0.08-0.22), similar TiO_2 (0.5-1.1 wt%), K/Rb (350-600), K/Ba (25-40), Ba/Rb (16-25) at the andesite range.

Compared to MORB, the modern IBM backarc basin volcanic rocks have slightly lower TiO_2, Zr, and Y contents but significantly higher K_2O, Rb, Ba, and Sr abundances (Figures 6-5A,B). However, both have similar range of trace element ratios of K/Ba (30-120), K/Sr (5-30), Ba/Rb (2-20), Rb/Sr (< 0.04), Ti/Zr (70-120) and Zr/Y (2-4) (Figures 6-5B,C). The majority of IBM modern backarc basin volcanic rocks have high K/Rb (500-1100) and Sr/Y (4-12) relative to those of MORB (K/Rb 200-600, and Sr/Y 2-5) (Figure 6-5B). The trace element behaviour of Daito Basin, West Philippine Basin and Shikoku Basin basalts is strikingly different (Figure 6-6). The Daito Basin basalts have the highest Rb (8-25 ppm), Ba (100-350 ppm), Sr (300-1000 ppm), TiO_2 (3.0-5.5 wt%) and Zr (150-350 ppm), while the West Philippine Basin basalts have the lowest Ba (< 50 ppm), Sr (70-120 ppm), TiO_2 (0.8-1.5 wt%), Zr (40-80 ppm) and slightly lower Y (20-30 ppm). The Shikoku Basin basalts have intermediate abundances of Ba (30-80 ppm), Sr (120-220 ppm), TiO_2 (1.0-2.2 wt%), Zr (80-160 ppm) and Y (25-40 ppm), similar to modern IBM backarc basin basalts.

Figure 6-7 shows the N-MORB normalised representative multi-element patterns for the averaged Leg 60 and Leg 125 glasses. Clearly, these patterns are similar. The abundances of LIL element such as K, Rb, Ba and Sr increase with the increase of SiO_2. The contents of HFS element such as Ti, Zr and Y of basaltic and basic andesitic glasses are generally close to the average N-MORB. The L60A group glasses are very similar to the L125 group glasses while L60B group glasses have significantly higher LIL element such as Rb, Ba and Sr relative to the L125-L60A glasses.

A comparison of selected trace element (Rb, Ba, Sr, Zr, Y) abundances and ratios among L125 glasses, Site 786 basement volcanic rocks, turbidites (A:18-35 Ma; B:0-17 Ma) and L60 glasses, Site 458 and 459B basement volcanic rocks, and modern Mariana volcanic rocks are shown in Figures 6-8A,B and C. It is clear that there is a significant difference between Mariana glasses and Mariana forearc basement volcanic rocks with the latter having very low Ba (< 100 ppm), Sr (60-160 ppm), Zr (25-50 ppm) and Y (< 10 ppm) and consequently high K/Ba (80-400), K/Sr (40-100), Zr/Y (3-6) and Rb/Sr (0.08-0.3), and low Ba/Rb (0.5-7) in the andesite range, all of which are characteristics of boninitic series (e.g., Pearce et al., 1992). The majority of Eocene-Oligocene IBM forearc basement volcanic rocks are of boninitic affinity with a tholeiitic minority (e.g., Taylor, 1992). The trace elements Rb, Ba, Sr, Zr, Y and their ratios of the forearc Eocene-Oligocene tholeiitic rocks do broadly overlap with the modern IBM arc volcanic rocks. The turbidites have very similar trace element compositions compared with the L125 glasses. Obvious differences are noted between the Izu-Bonin and Mariana arc volcanic rocks with the latter having higher LIL element abundances such as Rb, Ba, Sr but similar Zr and Y abundances.

6.4 Summary

Based on analyses of individual glass shards from DSDP Leg 60 and ODP Leg 125 for major elements (Ti, K) by EMP and selected trace elements (Rb, Ba, Sr, Zr, and Y) by PIXE-PMP, together with comparative studies of IBM glasses and IBM volcanic rocks, the following summary points can be made:

1. The ~ 220 individual glass shards studied are geochemically representative of volcanic glasses sampled from DSDP Leg 60 Site 458 and 459B and ODP Leg 125 Sites 782A, 784A and 786A. The trace element data indicate that LIL elements such as K, Rb, Ba, and Sr have peaks at ~ 20 Ma, 8-11 Ma, and ~ 2 Ma.

2. Abundances at specific SiO_2 content of trace elements such as Rb, Ba, and Sr like major element K_2O and CaO do show temporal and spatial chemical changes. The Izu-Bonin glasses (L125 glasses, 0-17 Ma) are very similar to older Mariana glasses (L60A glasses, 18-35 Ma), but significantly different from L60B glasses (0-17 Ma) in Rb, Ba, Sr abundances at a given SiO_2 content. The majority of L60B andesitic glasses have higher Rb (10-45 ppm), Ba (250-800 ppm), Sr (250-600 ppm), similar Zr (40-110 ppm), Y (20-40 ppm), Ga (8-20 ppm), Cu (10-250 ppm)

and Zn (70-160 ppm) relative to those of the majority of L60A and L125 andesitic glasses (Rb < 18 ppm, Ba 20-250 ppm, Sr 100-250 ppm, Zr 30-90 ppm, Y 15-35 ppm, Ga 8-20 ppm, Cu 10-250 ppm, Zn 70-160 ppm).

3. The L125 glasses have similar trace element compositions to the Izu-Bonin arc volcanic rocks with the exclusion of IwoJima. Generally, the Mariana Quaternary-Pliocene glasses (L60QP) are very similar to modern Mariana arc volcanic rocks in terms of Ba, Rb, Zr, and Y abundances but have lower Sr (200-350 ppm). Lower Sr abundances (200-500 ppm) in Late-Middle Miocene glasses relative to the arc volcanic rocks (400-1000 ppm) in andesitic bulk compositional range, possibly reflects plagioclase accumulation in the rocks.

4. It is clear that a medium-K characteristic is not synonymous with the calc-alkaline series.

5. From the view of characteristic trace element (Rb, Ba, Sr, Zr, and Y) abundances and ratios, the IBM volcanic glasses are clearly distinct compared with the Eocene-Oligocene IBM forearc basement volcanic rocks, the majority of which belong to the boninitic series. No boninitic glasses have been found in the ash layers, indicating the restriction of this type of magmatism to the early stages of arc evolution and/or a lack of subaerial explosivity. The existence of boninitic activity in the IBM arc system in the period ~ 45 to 30 Ma, and the absence of boninitic ashes shows that the arc was zoned across - strike.

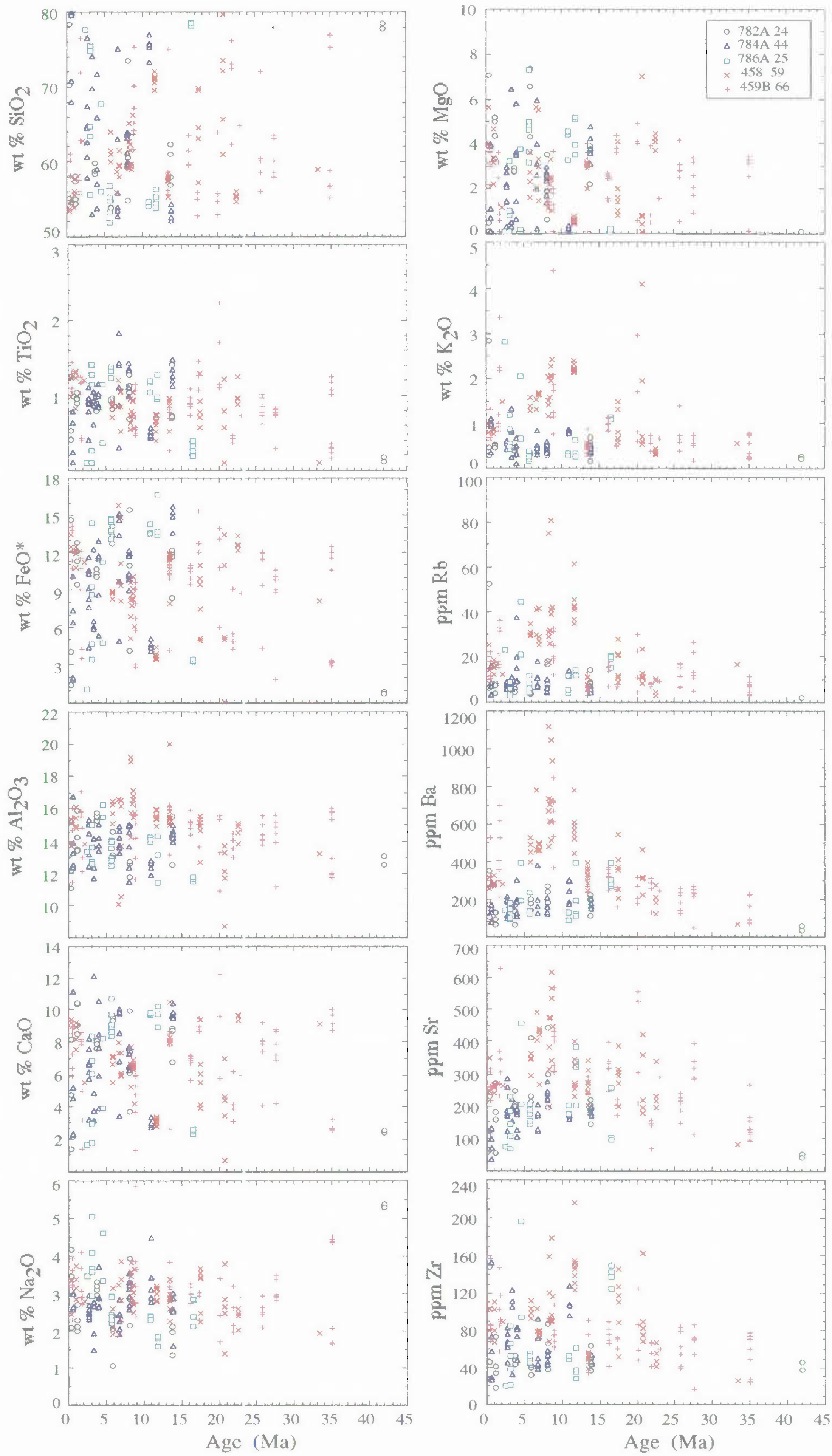

Figure 6-1A Comparison of compositions of individual glass shards from DSDP Leg 60 and ODP Leg 125 ash layers during the IBM arcs' evolution.

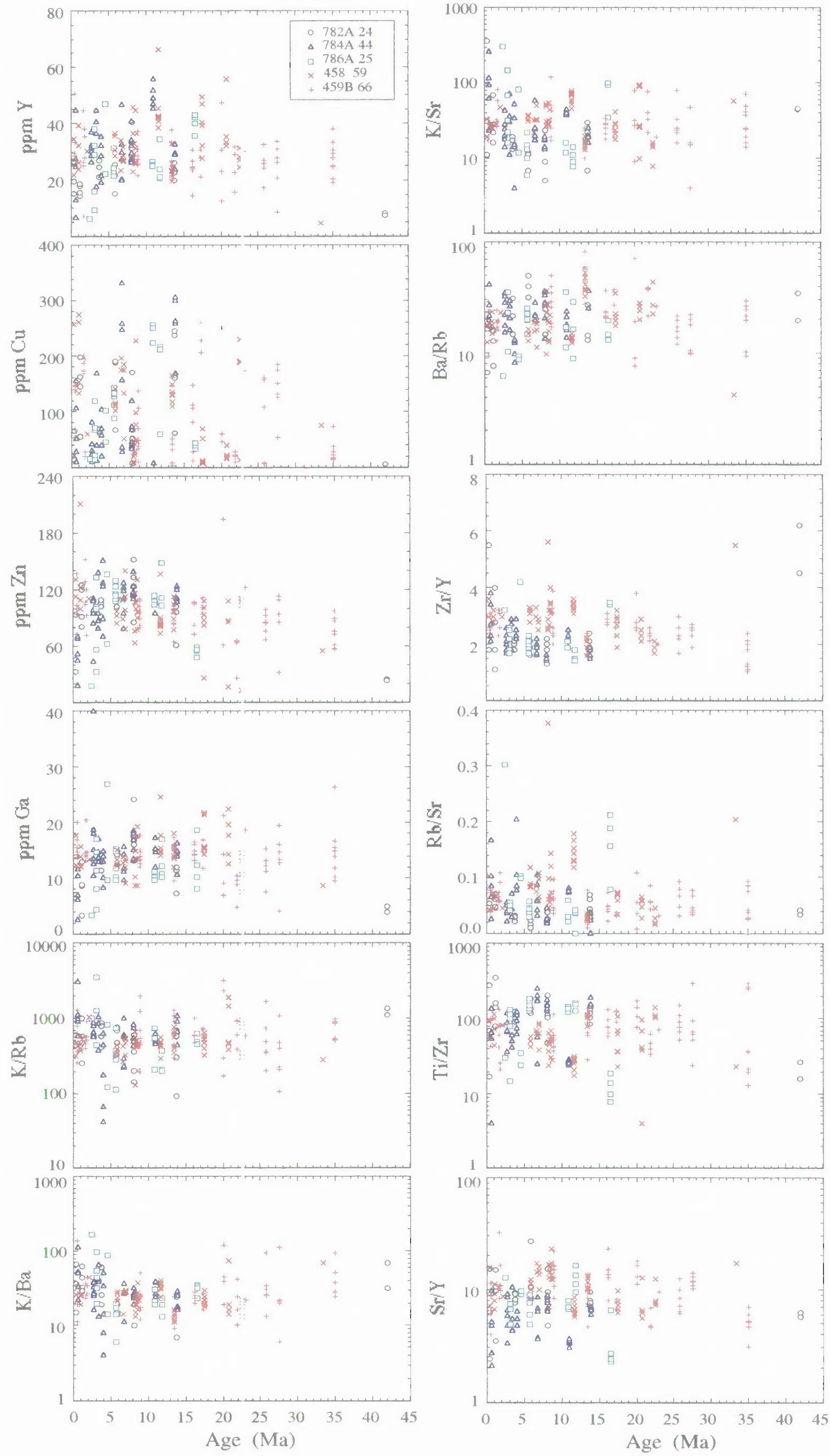

Figure 6-1B Comparison of compositions of individual glass shards from DSDP Leg 60 and ODP Leg 125 ash layers during the IBM arcs' evolution.

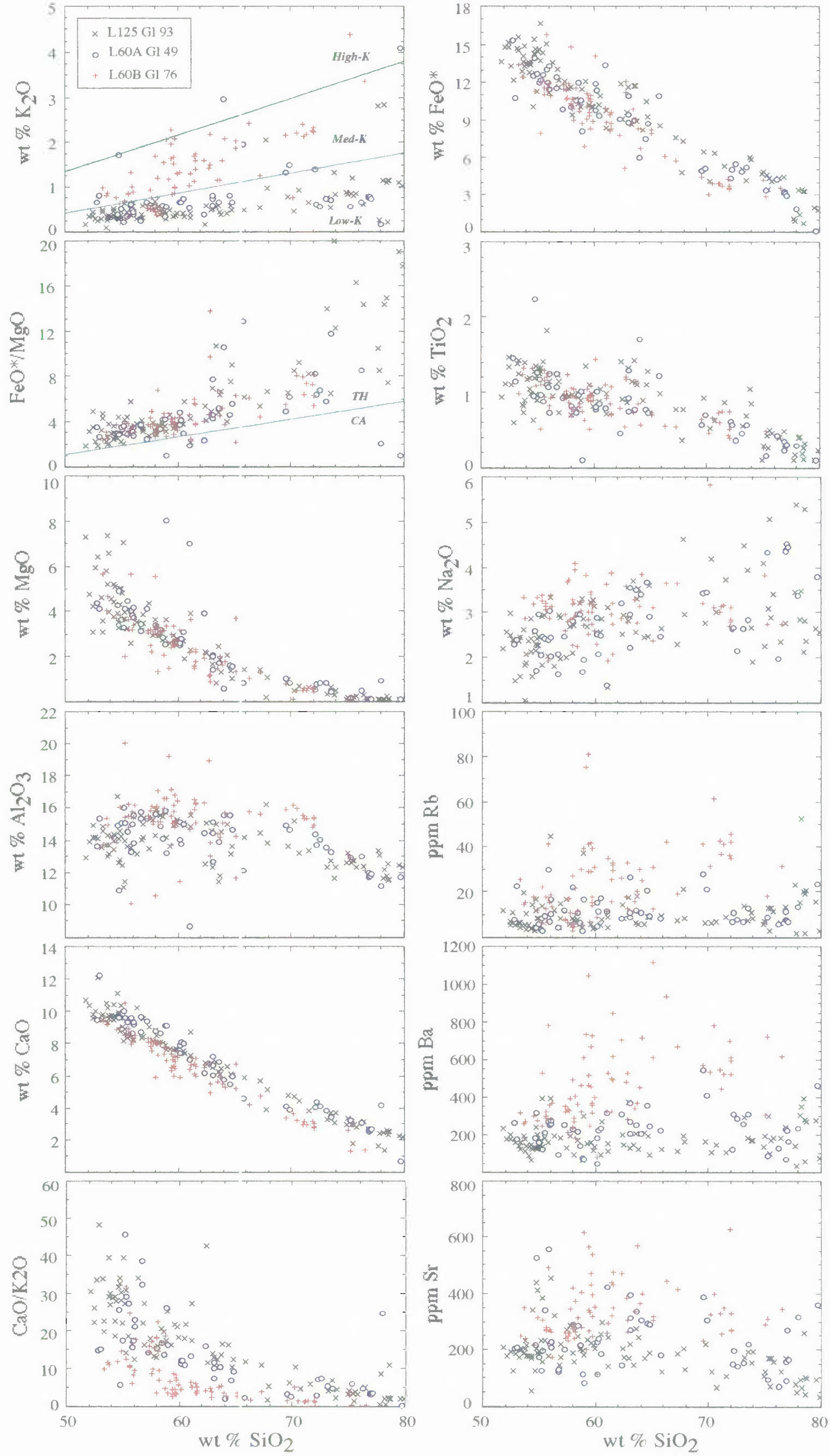

Figure 6-2A Comparison of compositions of individual glass shards in different age groups from Leg 60 and Leg 125 ash layers during the IBM arcs' evolution.

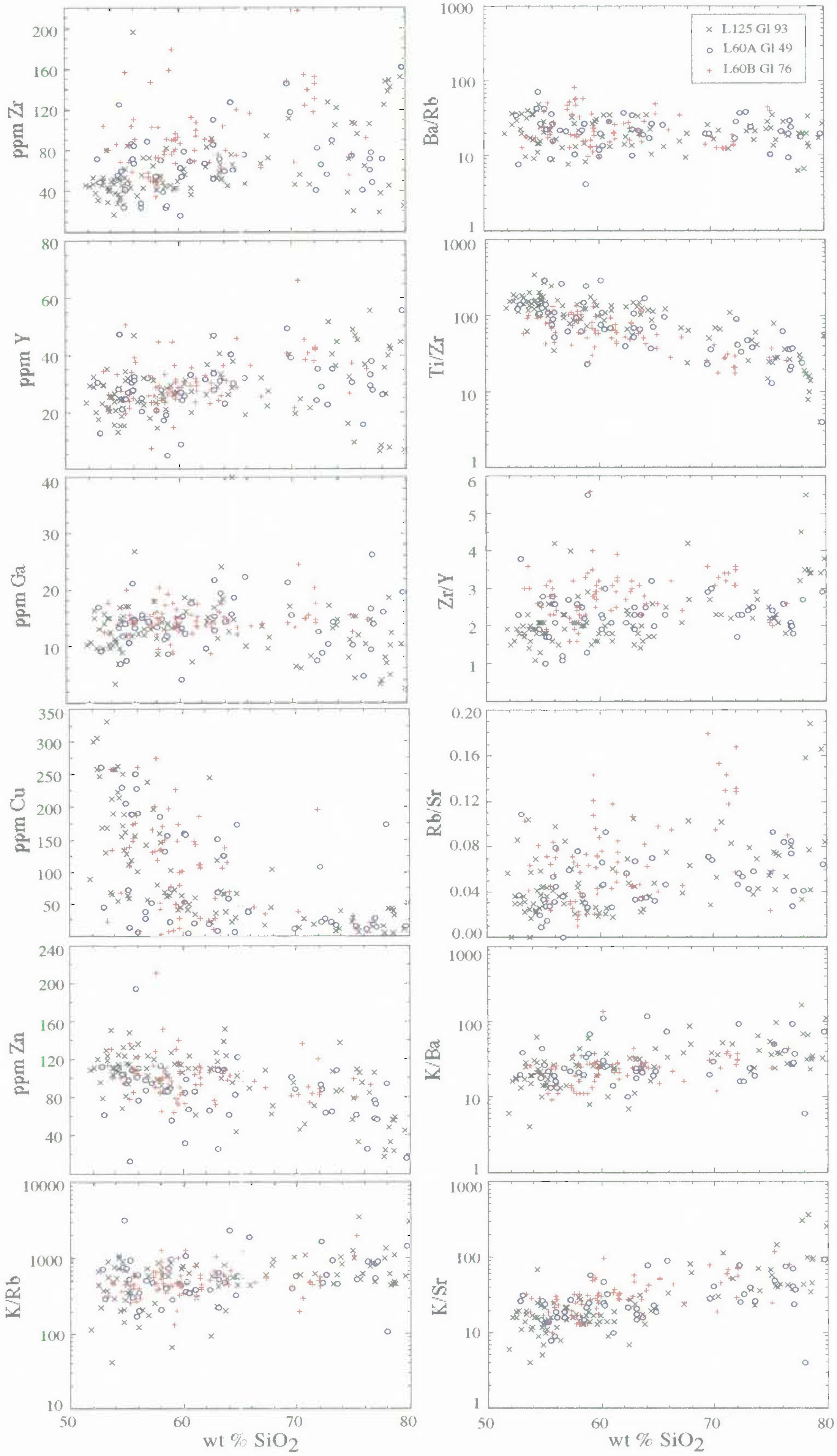

Figure 6-2B Comparison of compositions of individual glass shards in different age groups from Leg 60 and Leg 125 ash layers during the IBM arcs' evolution.

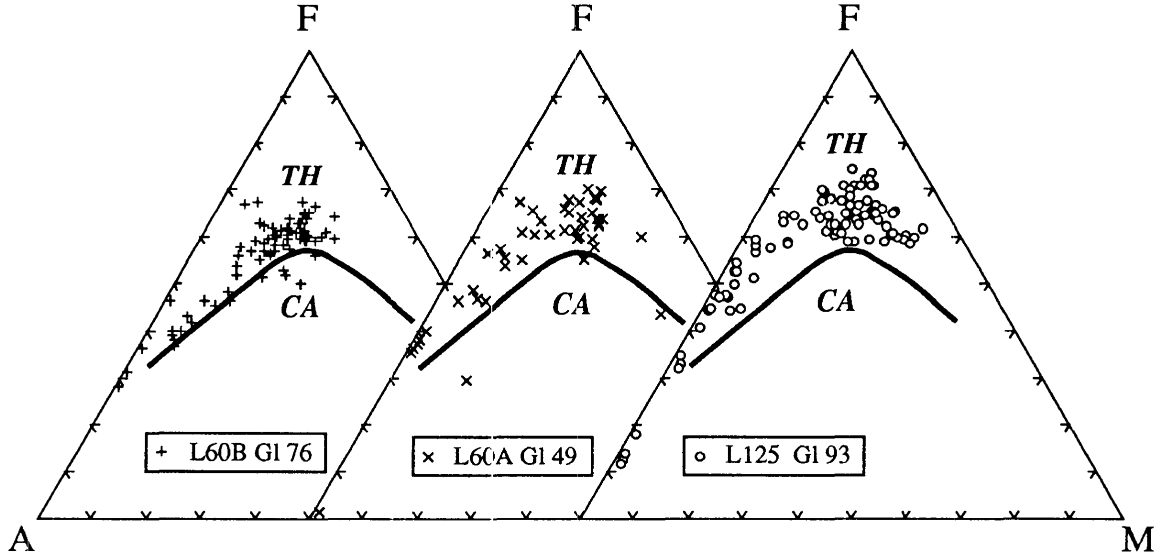

Figure 6-2C Comparison of AFM diagrams for three groups of individual glass shards from DSDP Leg 60 Sites 458 and 459B and ODP Leg 125 Sites 782A, 784A, and 786A ash layers . L60B Gl 76 is 76 point analyses of individual glass shards from DSDP Leg 60 Sites 458 and 459B, 0 ~ 17 Ma (present to Middle Miocene), L60A Gl 49 is 49 point analyses of glass shards from Leg 60 Sites 458 and 459B, 18 ~ 35 Ma (Early Miocene to Oligocene); L125 Gl 93 is 93 point analyses of individual glass shards from ODP Leg 125 Sites 782A, 784A, and 786A, 0 ~ 17 Ma. See text for discussion.

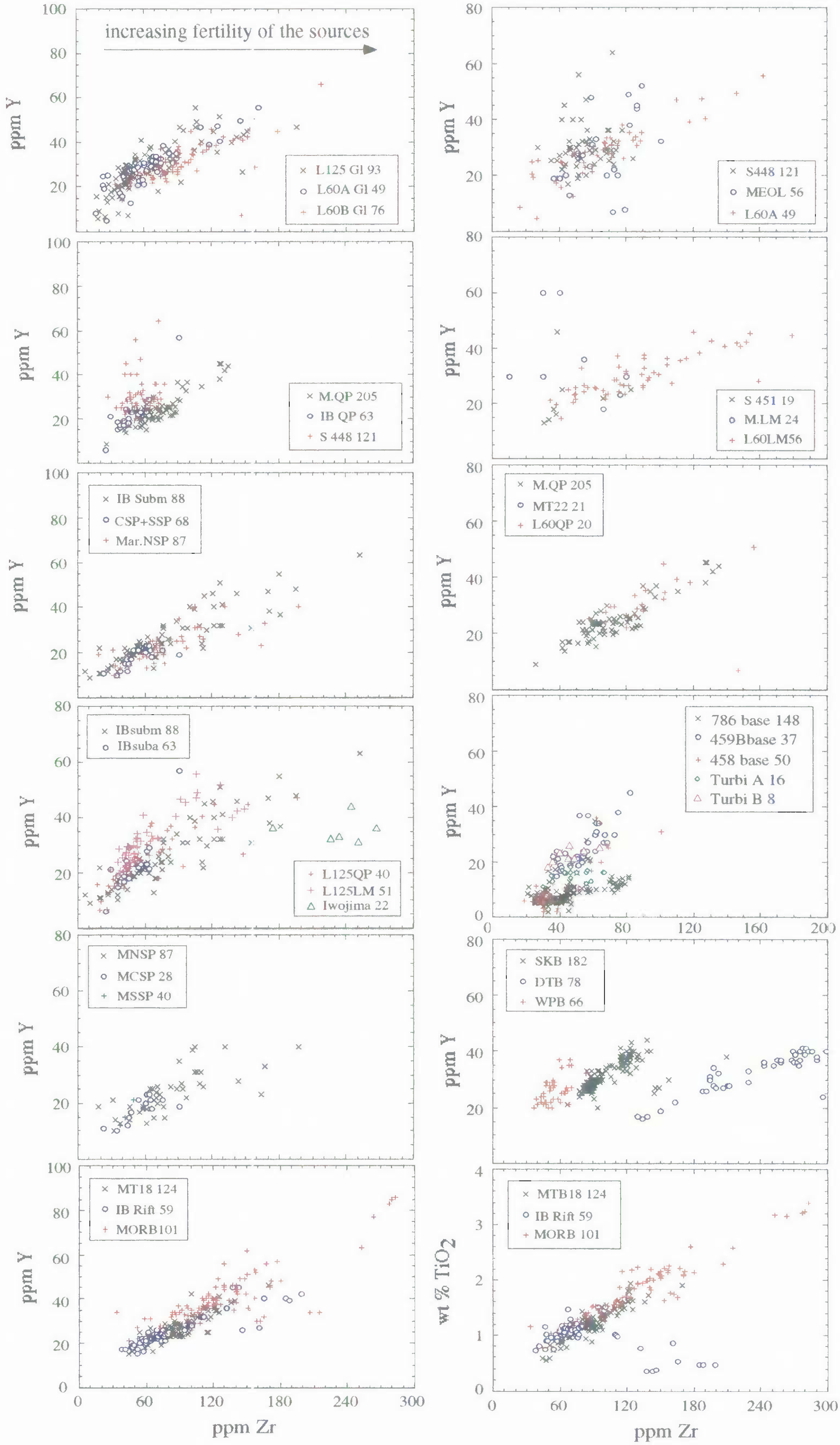

Figure 6-3 Comparison of compositions of glass shards from Leg 60 and Leg 125 ash layers with IBM arc and basin volcanic rocks and MORB.See text for data sources.

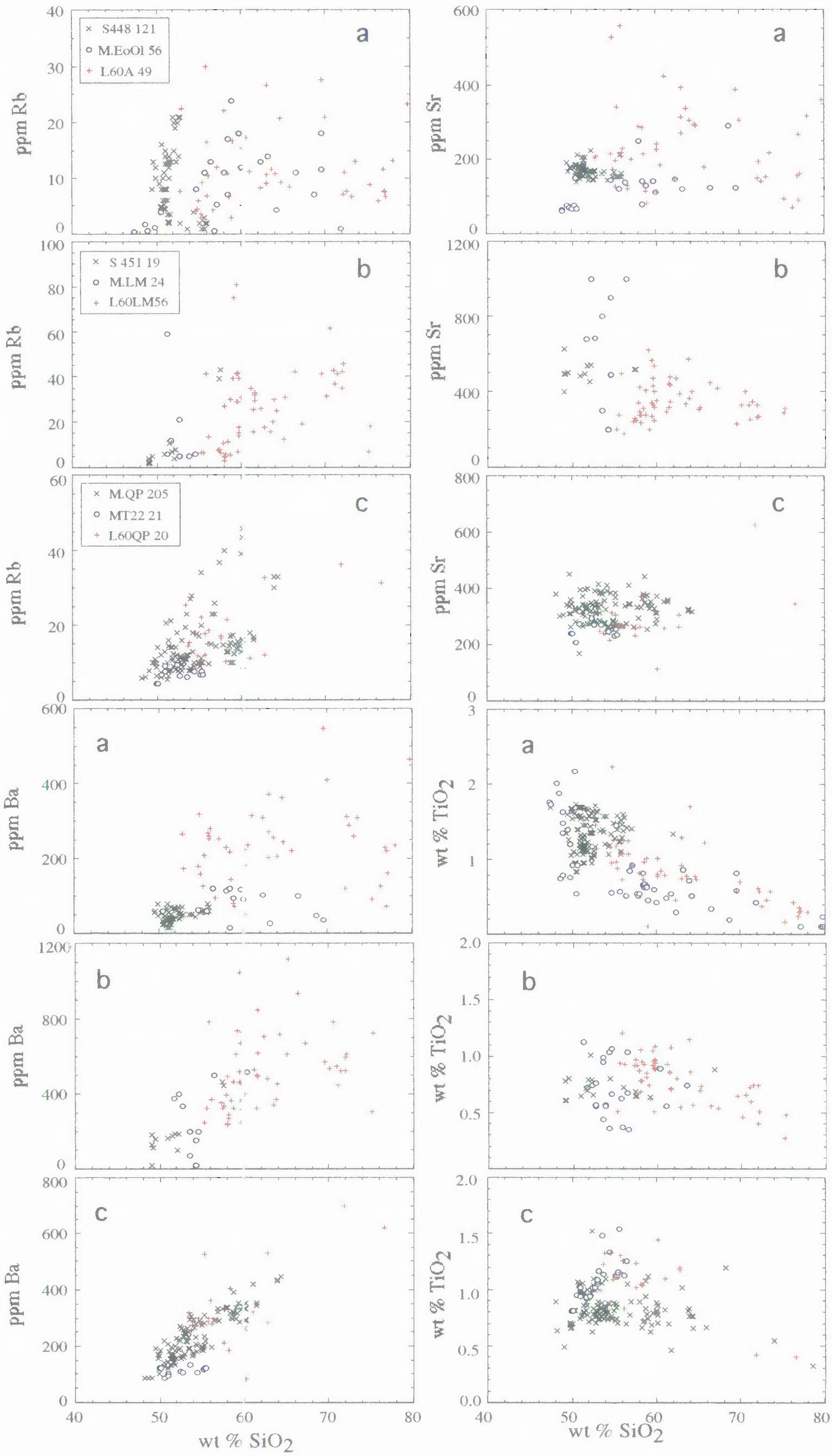

Figure 6-4A Comparison of compositions of individual glass shards from Leg 60 and Mariana arc volcanic rocks during the IBM arcs' evolution. See text for data sources.

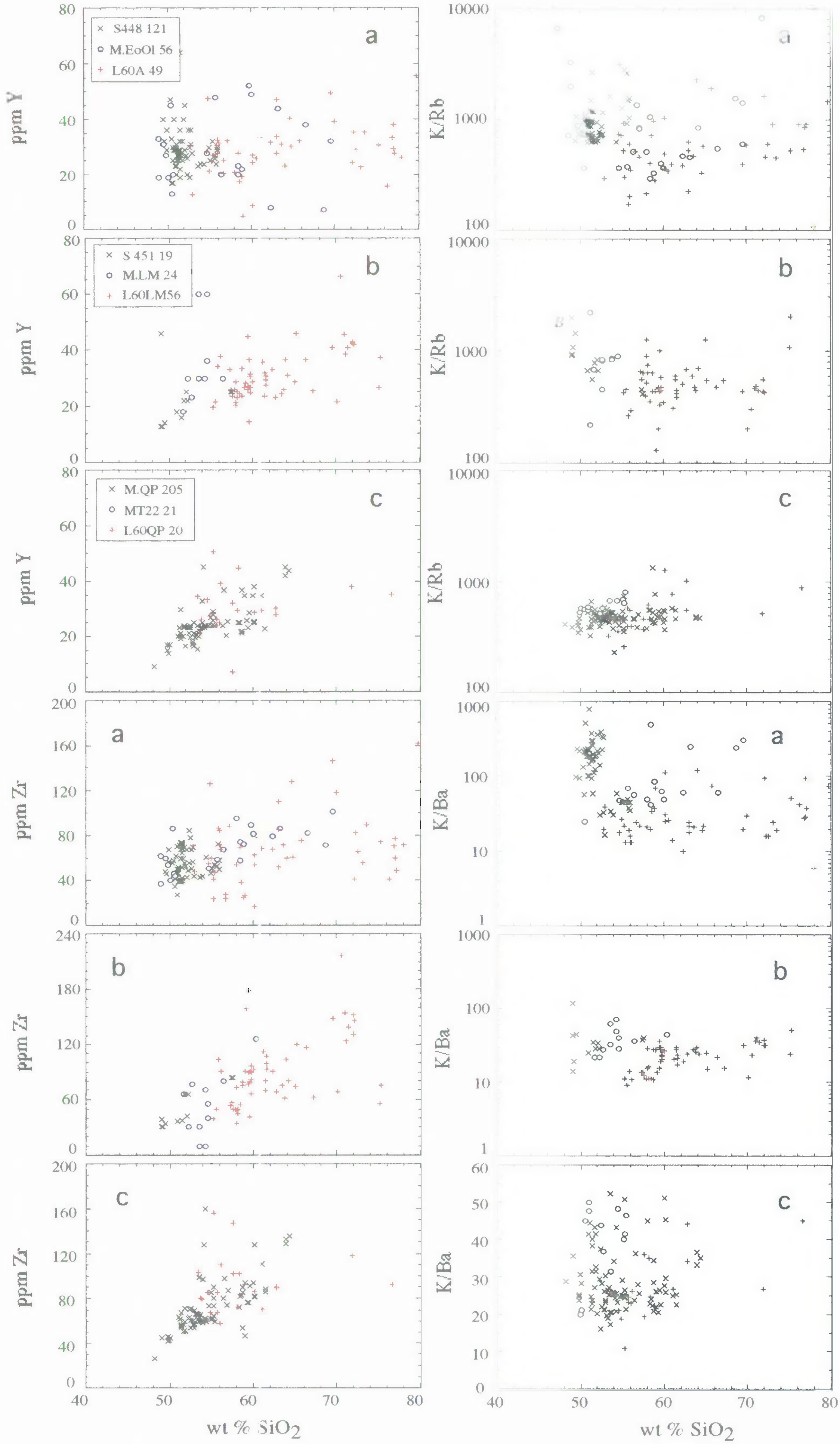

Figure 6-4B Comparison of compositions of individual glass shards from Leg 60 and Mariana arc volcanic rocks during the IBM arcs' evolution. See text for data sources.

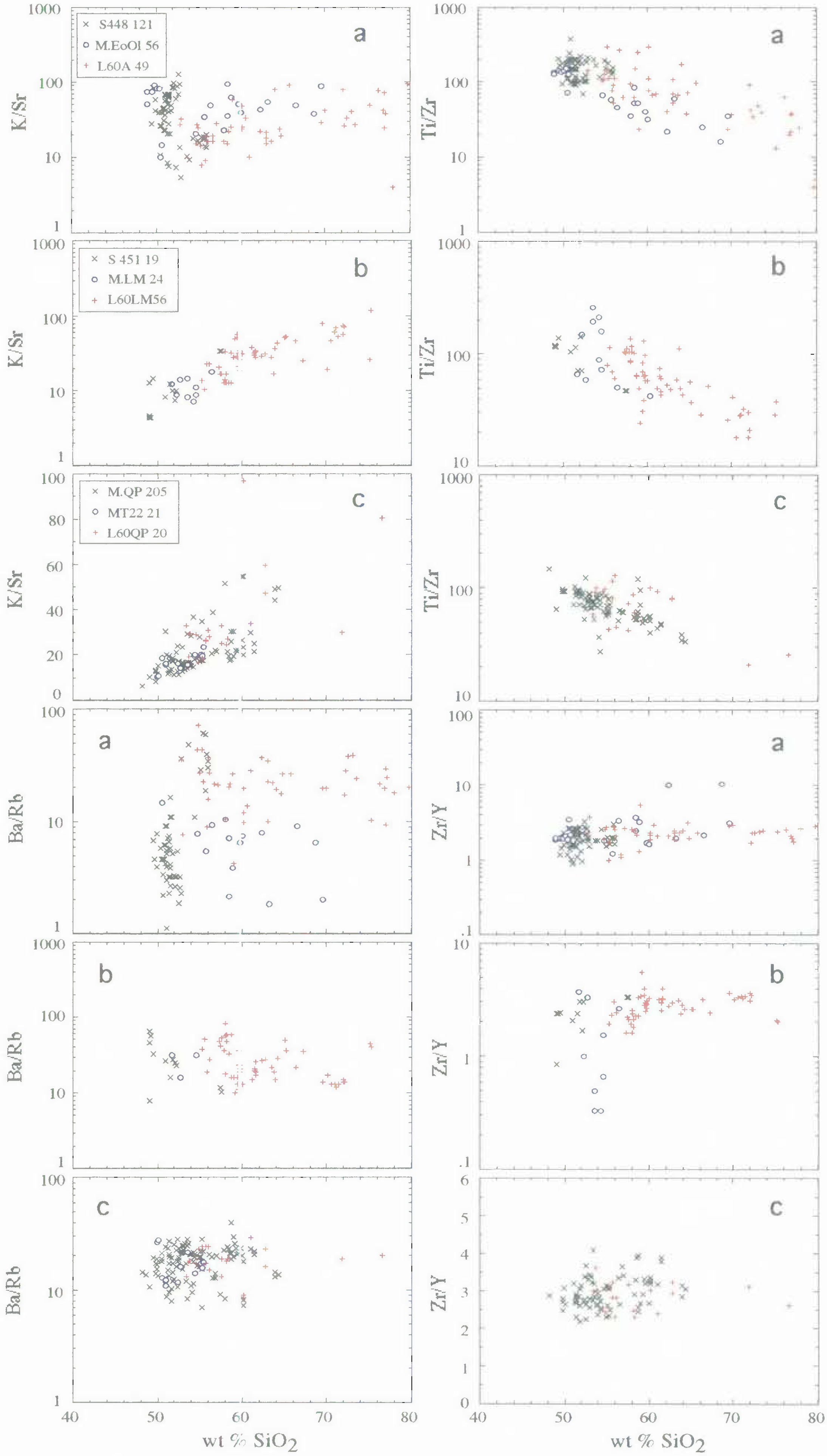

Figure 6-4C Comparison of compositions of individual glass shards from Leg 60 and Mariana arc volcanic rocks during the IBM arcs' evolution. See text for data sources.

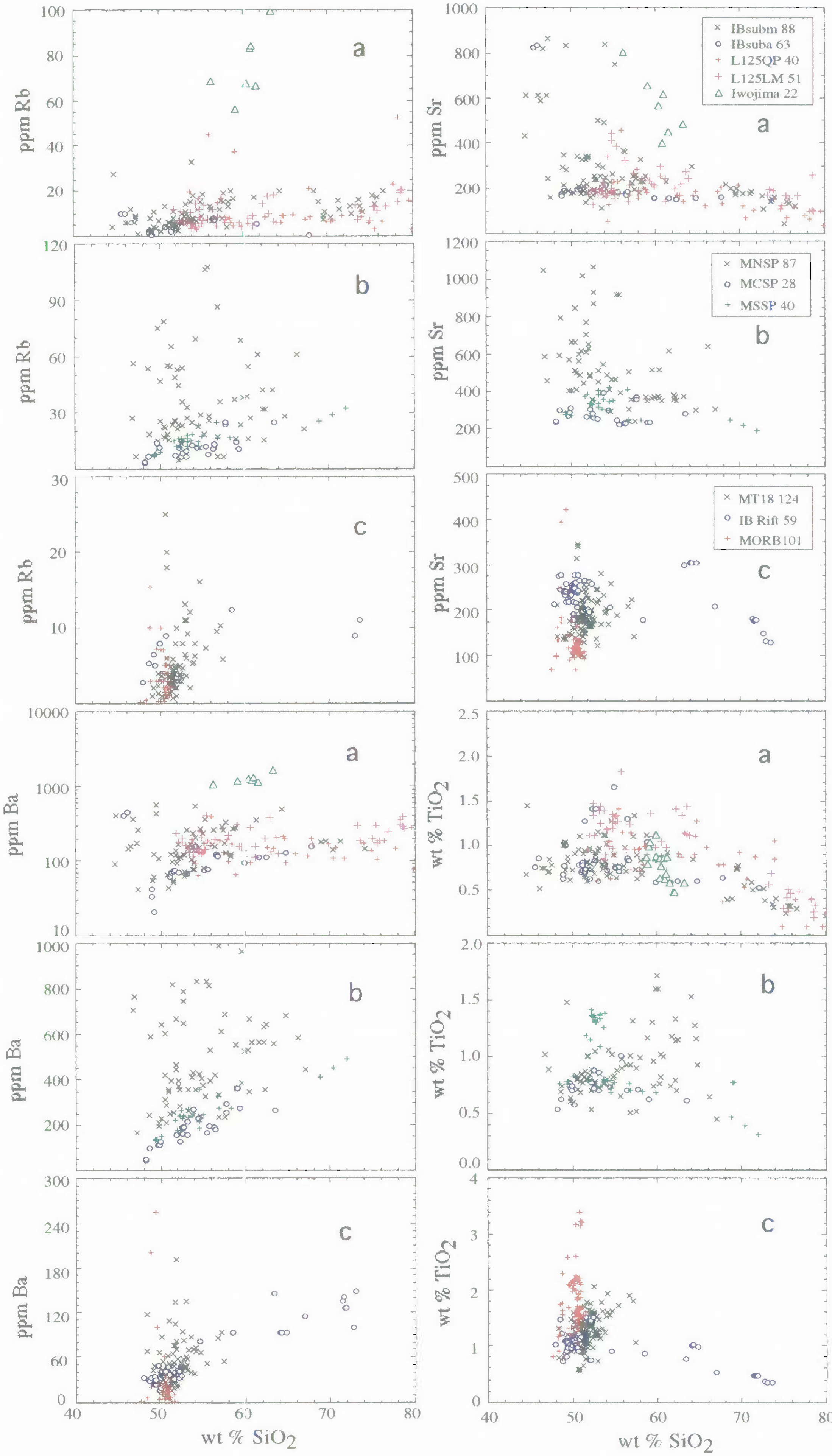

Figure 6-5A Comparison of compositions of individual glass shards from Leg 125 with IB arc volcanic rocks, IBM basin basalts and MORB. See text for data sources.

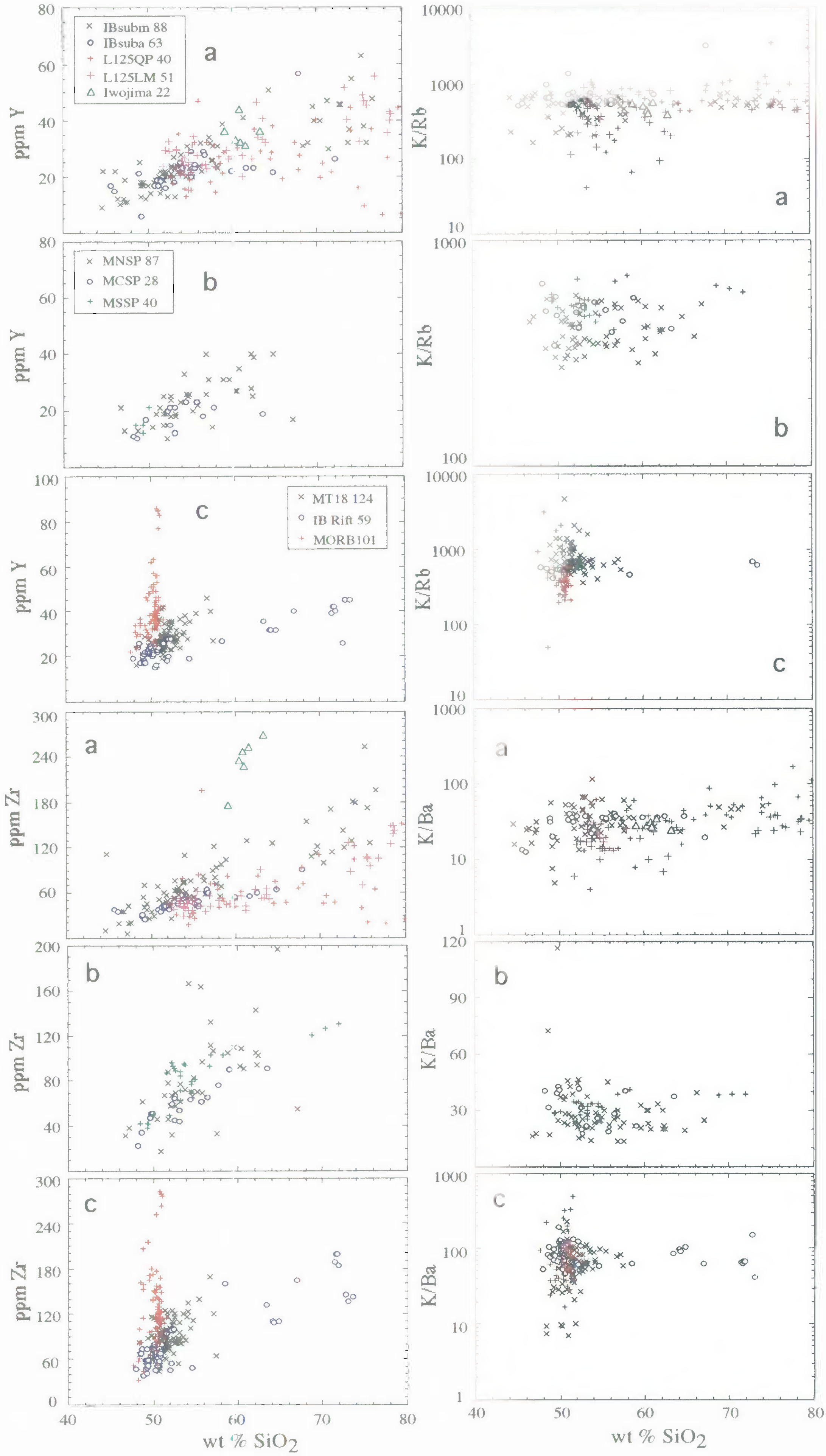

Figure 6-5B Comparison of compositions of individual glass shards from Leg 125 with IB arc volcanic rocks, IBM basin basalts and MORB. See text for data sources.

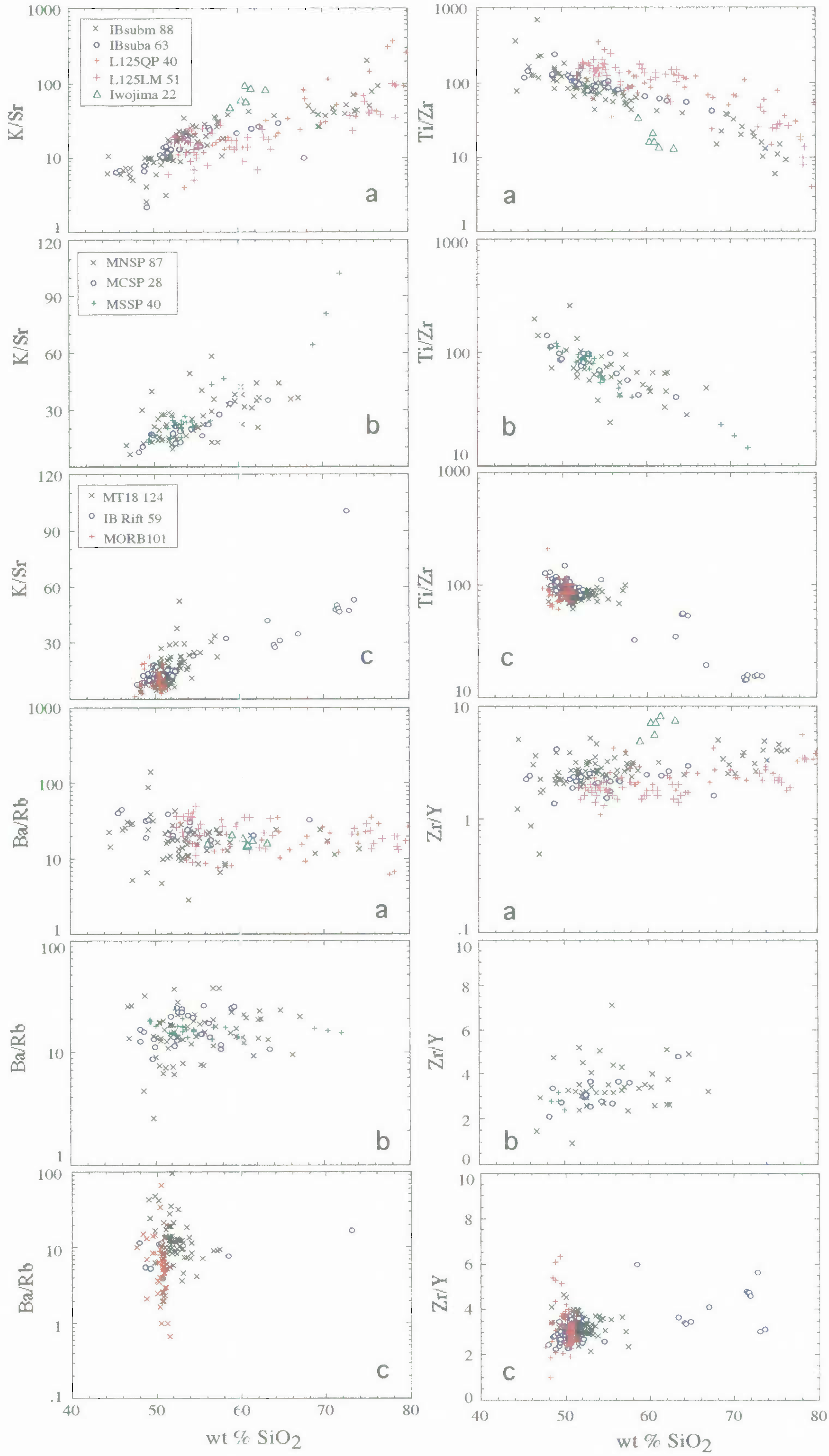

Figure 6-5C Comparison of compositions of individual glass shards from Leg 125 with IB arc volcanic rocks, IBM basin basalts and MORB. See text for data sources.

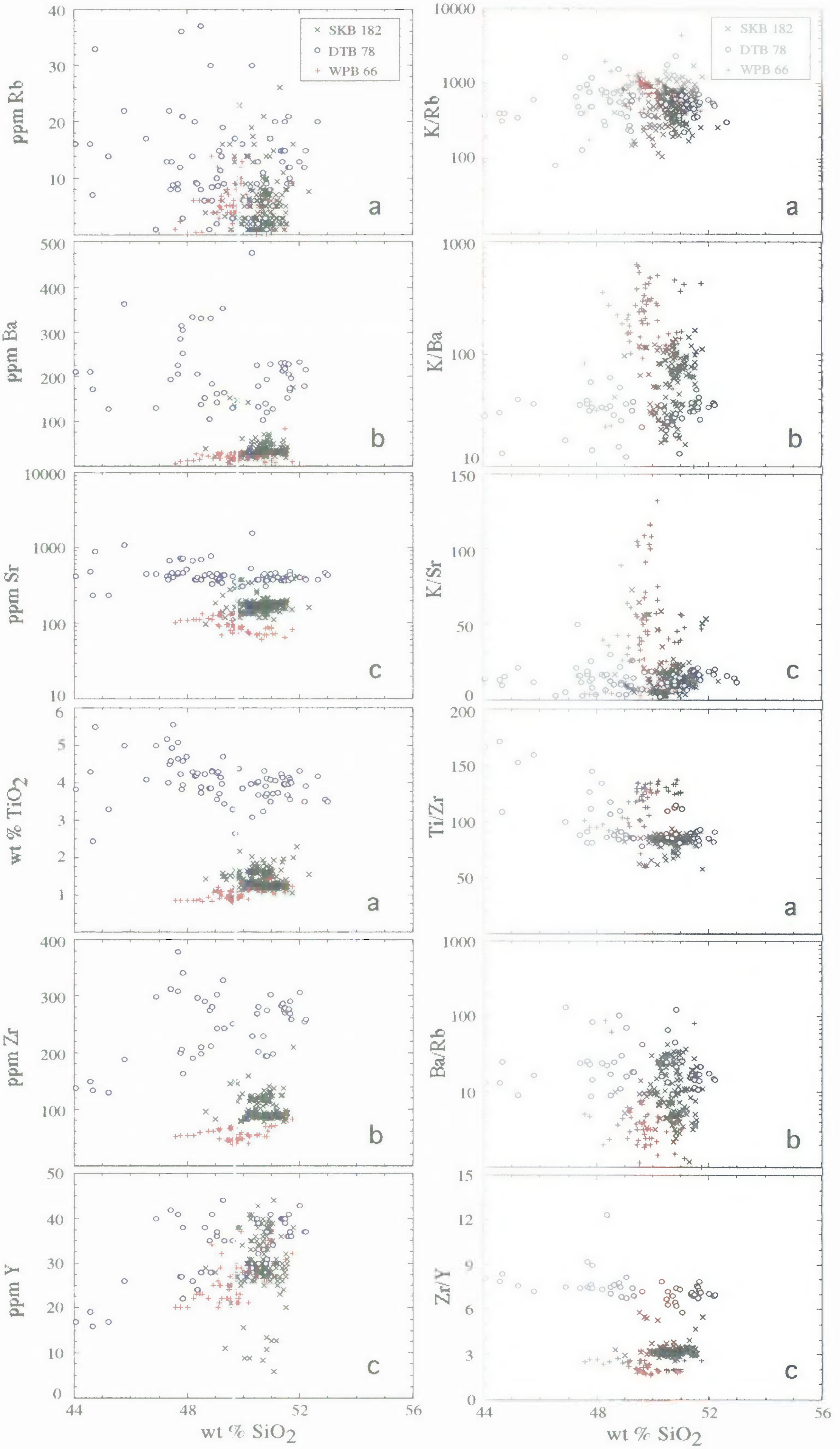

Figure 6-6 Comparison of compositions of basin basalts from Daito basin, West Philippine basin and Shikoku basin. See text for data sources and legends.

N-MORB normalised multi-element patterns

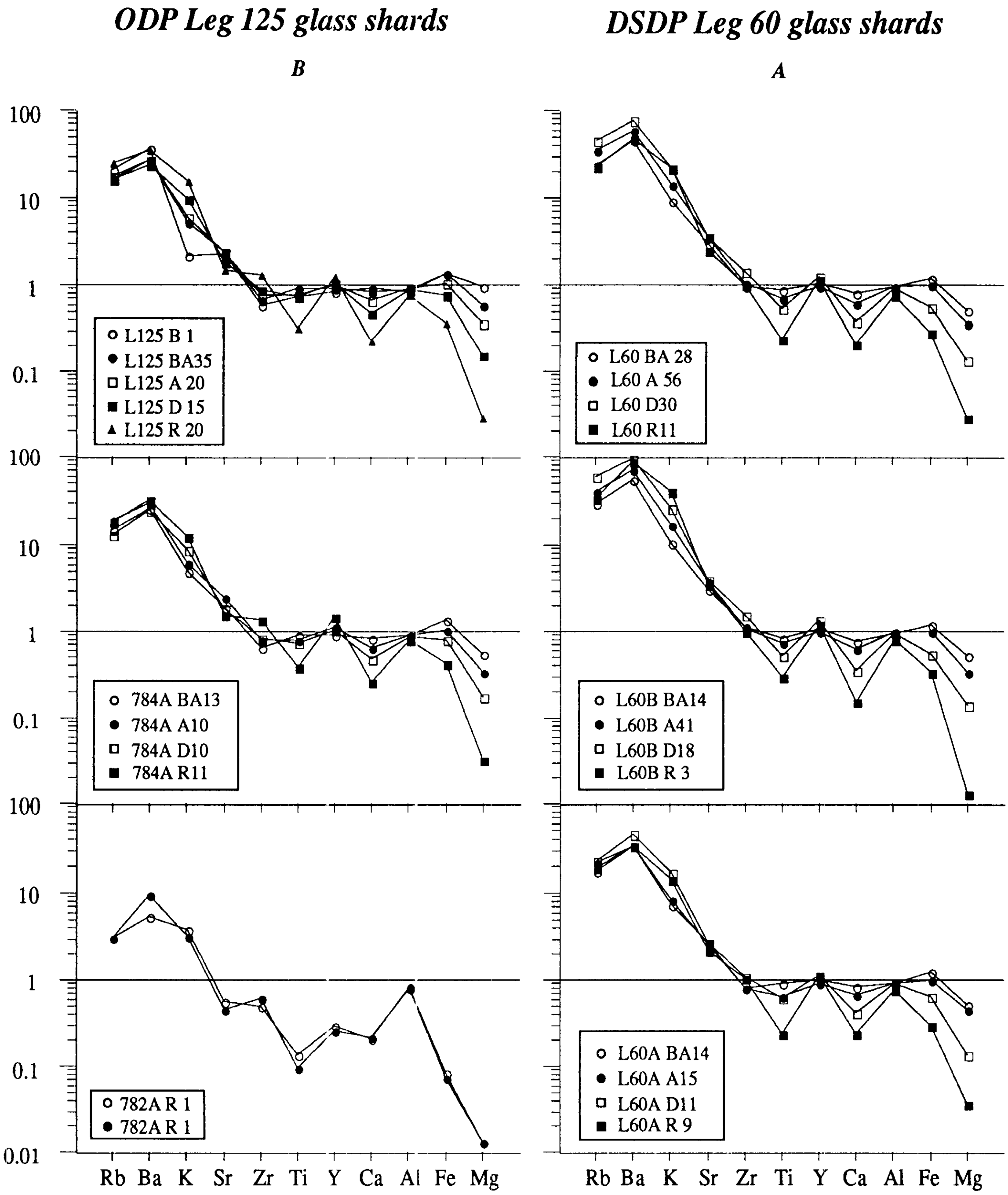

Figure 6-7 N-MORB normalised abundances of individual glass shards from DSDP Leg 60 (A) and ODP Leg 125 (B). Notation by the specific sample symbols is Leg or Site number followed by compositional type (B-basalt, BA-basaltic andesite, A-andesite, D-dacite, R-rhyolite) and analysis number for average. L60B is a time period of 0 ~ 17 Ma (present to Middle Miocene); L60A is a period of 18 ~ 35 Ma (Early Miocene to Oligocene); L125 is a time period of 0 ~ 17 Ma; 782A R1 is a rhyolitic glass, Eocene (~ 42 Ma). The normalising values of Rb, Ba, K, Sr, Zr, Ti, and Y are from Sun and McDonough (1989), Ca, Al, Fe, and Mg, from the average of 397 MORB glass samples collected in this work. See text for discussion.

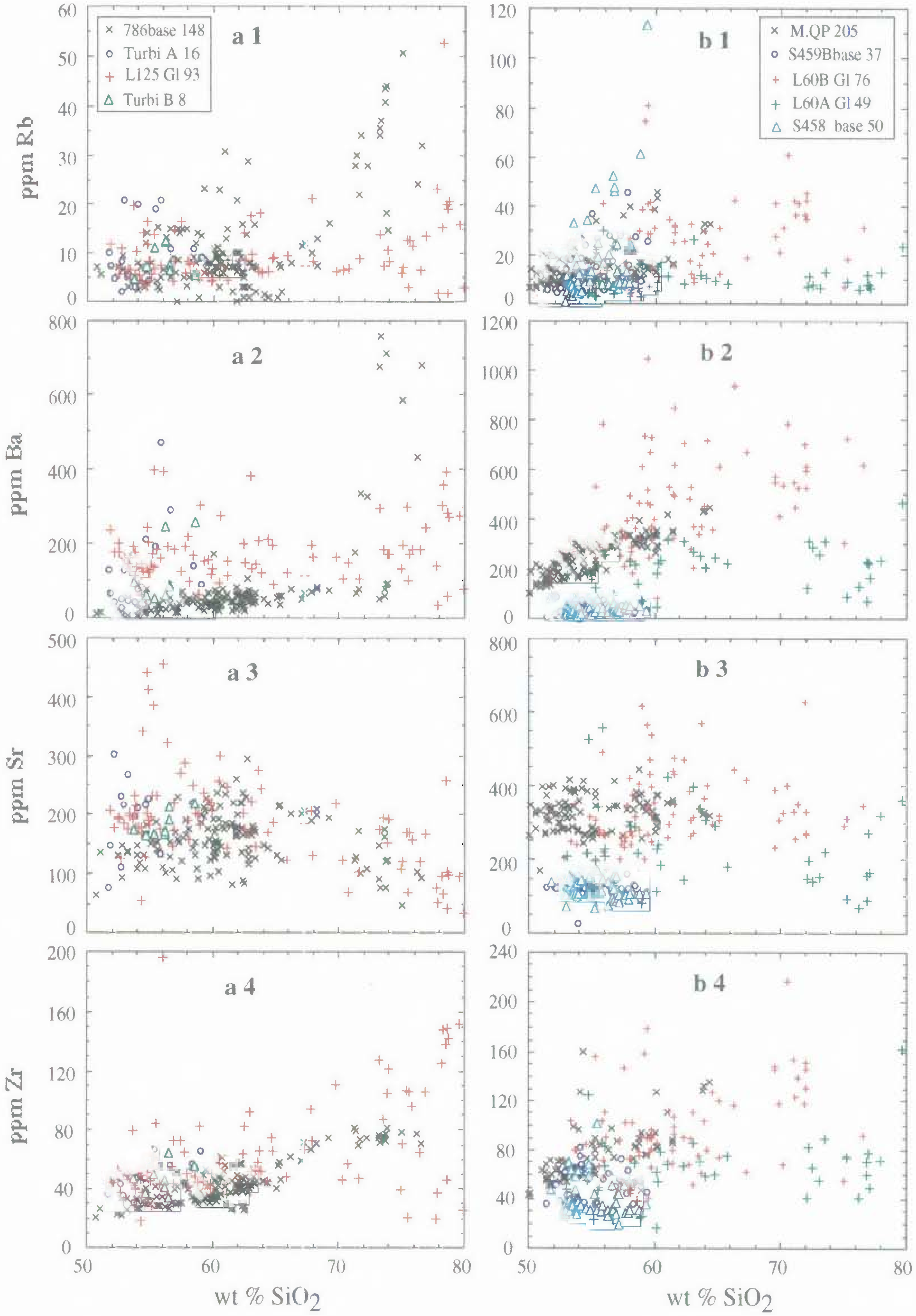

Figure 6-8A Comparison of compositions of individual glass shards from DSDP Leg 60 and ODP Leg 125 ash layers with drilled basement volcanic rocks of the Izu-Bonin and Mariana forearc (786base 148, 148 analyses of ODP Leg 125 Site 786 basement volcanic rocks; S458base 50 and S459Bbase 37, 50 and 37 analyses of DSDP Leg 60 Site 458 basement and 459B basement volcanic rocks respectively), turbidites recovered from ODP Leg 126 forearc Sites (Turbi A 16 and Turbi B 8, 16 and 8 analyses of turbidites from 18 ~ 30 Ma and 0 ~ 17 Ma respectively) and Mariana modern volcanic rocks (MQP 205). See Figure 6-2C for glass samples and text for data sources and discussion.

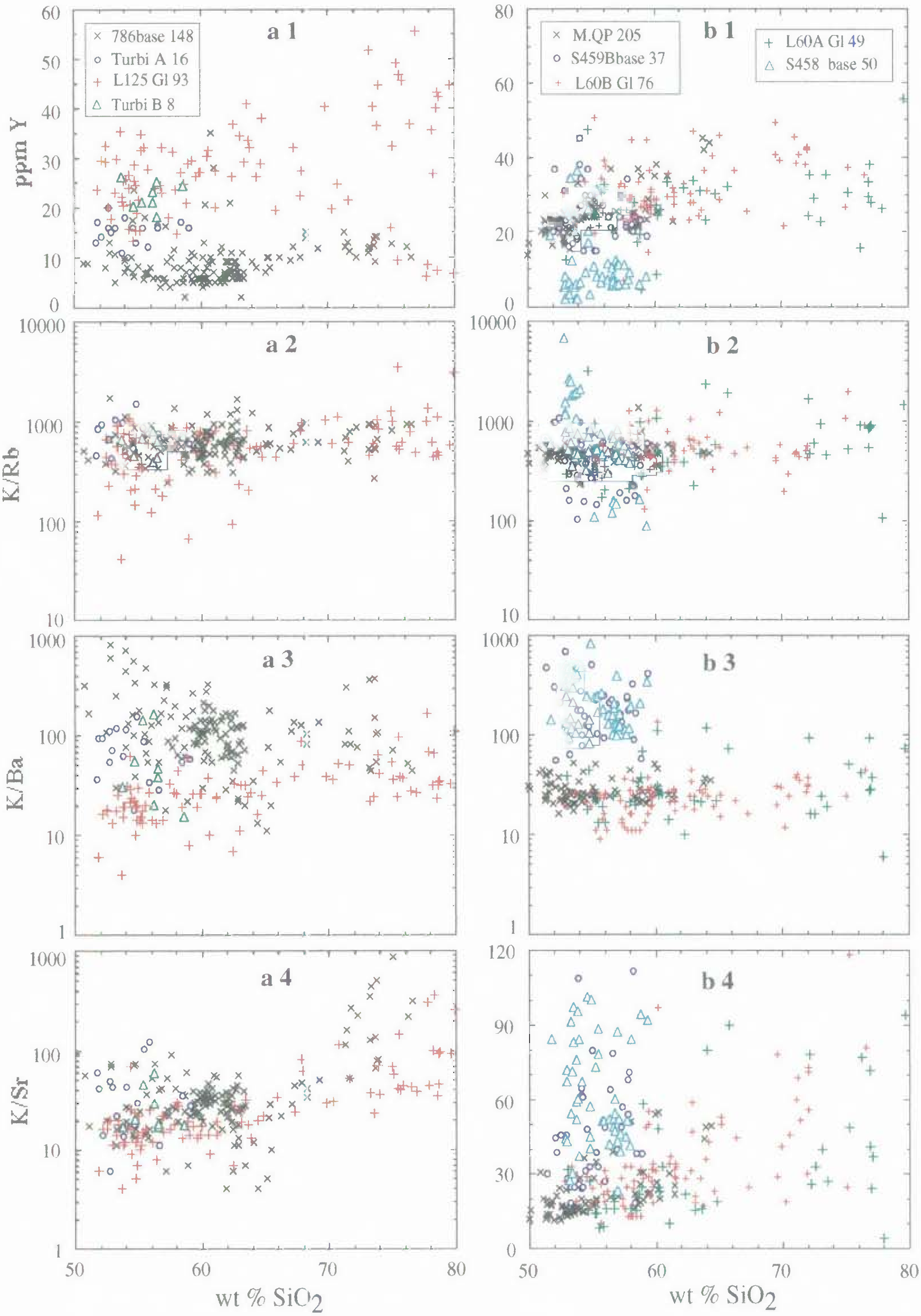

Figure 6-8B Comparison of compositions of individual glass shards from DSDP Leg 60 and ODP Leg 125 ash layers with drilled basement volcanic rocks of the Izu-Bonin and Mariana forearc (786base 148, 148 analyses of ODP Leg 125 Site 786 basement volcanic rocks; S458base 50 and S459Bbase 37, 50 and 37 analyses of DSDP Leg 60 Site 458 basement and 459B basement volcanic rocks respectively), turbidites recovered from ODP Leg 126 forearc Sites (Turbi A 16 and Turbi B 8, 16 and 8 analyses of turbidites from 18 ~ 30 Ma and 0 ~ 17 Ma respectively) and Mariana modern volcanic rocks (MQP 205). See Figure 6-2C for glass samples and text for data sources and discussion.

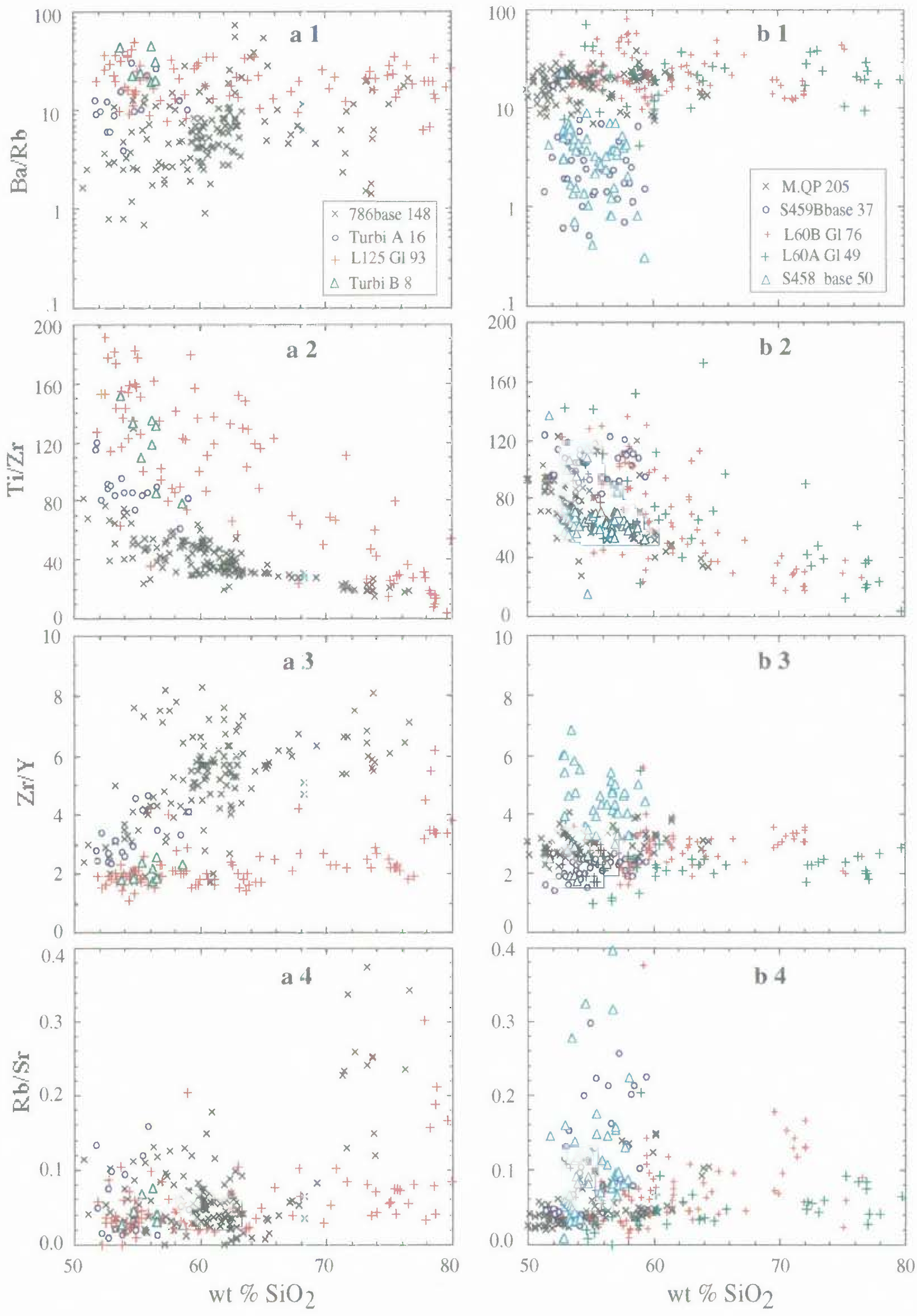

Figure 6-8C Comparison of compositions of individual glass shards from DSDP Leg 60 and ODP Leg 125 ash layers with drilled basement volcanic rocks of the Izu-Bonin and Mariana forearc (786base 148, 148 analyses of ODP Leg 125 Site 786 basement volcanic rocks; S458base 50 and S459Bbase 37, 50 and 37 analyses of DSDP Leg 60 Site 458 basement and 459B basement volcanic rocks respectively), turbidites recovered from ODP Leg 126 forearc Sites (Turbi A 16 and Turbi B 8, 16 and 8 analyses of turbidites from 18 ~ 30 Ma and 0 ~ 17 Ma respectively) and Mariana modern volcanic rocks (MQP 205). See Figure 6-2C for glass samples and text for data sources and discussion.