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GEOCHEMISTRY OF OCEANIC IGNEOUS ROCKS -- RIDGES AND ISLANDS

by

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Notes and summary for data examined for the paper "Zinc, copper, and lead in mid-ocean ridge basalts and the source rock control on Zn/Pb in ocean-ridge hydrothermal deposits" by Bruce R. Doe to appear in Geochimica et Cosmochimica Acta, in press, 1993.

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INTRODUCTION

In working on the subject paper, I was surprised at the lack of computerized data files available for the geochemistry of oceanic igneous rocks. Thus the accompanying data file, compiled from the published literature, is being made available to help rectify the situation. This data file, however, is not meant to eliminate reading the original papers but to eliminate the wasted time in searching for papers and entering data.

NOTES TO DATA

The Data File was compiled in a LOTUS 1-2-3, version 2.3, spreadsheet, a DOS program, using the .WK1 extension on an IBM PC compatible computer. The computer had a VGA graphics board. The spreadsheet consumes 529,422 bytes of memory and expanded memory may be needed if run in DOS.

The Data File covers the principal major elements: SiO_2, Al_2O_3, Fe_2O_3(T), MgO, CaO, Na_2O, K_2O, P_2O_5, and MnO, in that order when given. (T) means total Fe is expressed as ferric Fe. For convenience, a column for total Fe as ferrous Fe is also included along with data on ferrous and ferric Fe contents when published. Loss on ignition (LOI), H_2O, or H_2O- is included when any of these are given.

In addition, the following trace element contents are included when given: Zn, Cu, V, Cr, Ni, Zr, (MAJOR ELEMENTS), Sr, Ba, Sc, Ce, and Pb(ID)(where ID means determination by the isotope dilution technique). I also calculate V/Zn, Cu + Ni, and Fe + Ti when such information exists.

Selection of Data: Criteria used for selection, in addition to simply discovering a paper, were that the major elements and either Zn or Cu (preferably both) had to be available, not necessarily in the same paper. Also an attempt was made to obtain some data on

Mid-Ocean Ridge Basalts and Oceanic Islands Basalts (OIB) for the three largest oceans. Lastly, hybrid environments were included (e.g., Walvis Ridge/Rio Grande Rise in the South Atlantic Ocean Basin and Galapagos Rise in the Pacific Ocean Basin) where a blend of ridge and island volcanic rocks exist. MORB data from the South Atlantic may contain an island (hot spot) influence from the Tristan da Cunha hot spot. Basalts from the vicinity of the Famous area are thought to be influenced by the Azores hot spot, and data from the vicinity of the Galapagos hot spot may be influenced by that hot spot.

The terminology of MORB is becoming increasingly complex as more data are obtained. Normal MORB or N-MORB is used as defined by Frey et al. (1980)(also see papers cited therein): K~1000 ppm, Sr~130 ppm, Ba~10 ppm, $^{87}Sr/^{86}Sr_i<0.703$, and chondrite-normalized REE abundances are relatively depleted in light REE. $\epsilon(^{143}Nd/^{144}Nd)$ should be positive. Enriched MORB or E-MORB is higher in all these elements and isotope ratios. Transitional MORB or T-MORB is intermediate between N-MORB and E-MORB. Plume MORB or P-MORB is essentially similar to oceanic island basalts.

It should be emphasized that whereas data in the file have been carefully proofread for entry errors, typos in the published data may exist for a number of reasons. Although many authors were contacted in regard to explanations of outliers in trace element data, many did not respond, others said the reasons for the outliers were not known, and a few said that contamination to explain the outliers could not be ruled out.

The magnesium number (Mg #) is molar (Mg/(Mg + Fe) where Fe is ferrous iron and 10% of the total Fe is assumed to be ferric iron in the "calculated" column. In the "published" column, the Mg # is given as published. There is no standard way for calculating Mg #. To assume that 10% of the total iron is ferric iron is common, but other common assumptions are that 15% of the total iron is ferric, that 0% is ferric, or that the determined ferrous iron is used. The formula used is left in the calculation column for easy conversion to your preferred value. There is also no standard way of reporting Fe, particularly in that only some papers report both ferrous and ferric Fe (or ferrous/ferric values and total Fe). Thus columns are present both for total Fe as ferric and ferrous. The conversion factor from ferrous to ferric is to multiply by 1.111. One can easily tell what was in the original paper by looking at the ferrous and ferric columns.

Some papers quote analyses recalculated to a water-free basis, others give loss-on-ignition (LOI), others give H2O+ and H2O-, and many give nothing on water. If water data are needed, it is important to refer to the original papers (e.g., for calculation of norms, etc.).

The convention used when elements are below detection is to enter half the value of the detection limit. No special notation is made of these estimates.

References are not in any standard format, but enough information is given so one may recover the reference. Journal abbreviations are: Chem.Geol.- Chemical Geology; Contrib.- Contributions of Mineralogy and Petrology; EPSL-Earth and Planetary Science Letters; GSA Bull.- Geological Society of America Bulletin; Geol. Soc.- Geological Society (London); JGR-Journal of Geophysical Research; J.Pet.- Journal of Petrology.

Geographic abbreviations are: EPR- East Pacific Rise, MAR- Mid-Atlantic Ridge, de Fuca- Juan de Fuca.

Rarely is any information on analytical techniques or uncertainties given in the Data File.

The Data File was constructed to allow easy use in the plotting and regression program ISOPLOT, version 2.03, by K. Ludwig, 1990, U.S. Geological Survey Open-File Report 88-557, 45p. Thus cell widths are restricted to 9 characters.

Average values for geographic units incorporate all analyses. In some cases restricted localities are overrepresented (e.g., the FAMOUS area). Data in Czamanske and Moore (1977) appear to be included in a larger list of data by Bryan et al. (1979) with minor changes. Because the Czamanske and Moore (1977) paper is used in the subject paper for this data bank, the data by Bryan et al. (1979) are not included. Serocki volcano was first subdivided into 3 subgroups of analyses: two from core and dredge samples by the same laboratory, another for core samples by a second laboratory. Then the subgroups were averaged. Individual analyses for Serocki volcano are given at the bottom of the file. The data labeled as the Kane fracture zone on the Mid-Atlantic Ridge are also averages given in the paper by Bryan et al. (1981). To prevent undue duplication, only data on whole rocks is given for the Southeast Indian Ridge system (Klein et al., 1991) in the upper part of the table that averages are derived from. Data on glasses from many of the same samples are given at the bottom of the table to permit further evaluation of the differences to be expected between glass and whole rock. Cu, for example, averages remarkably the same value where data on glass-whole rock pairs are given (64.4 ppm vs. 63.5 ppm, respectively), although the glass is reported to contain 19% more Cu than the whole rock, in one case.

In other cases, a few outlying analyses are omitted that would unduly weight the averages; however, many Ocean Drilling Program sites involve basalts that have undergone submarine weathering. Cu can be mobile during such weathering but doesn't seem to move far. Note the Indian Ocean average for Cu is not unusual. There is a good bit of redundancy in data for the FAMOUS area. Langmuir et al. (1977) also seem to have analyzed three pieces from the same core as Bryan et al. (1979) with differences in Cu contents and in other trace metals by as much as 25%. Both sets of analyses were obtained by optical spectrometry. Bryan et al. (1979) analyzed carefully handpicked glass and Langmuir et al. whole rocks which exceeded 90% glass. Bryan et al. (1981) state that they find the largest difference between glass rims and crystalline interiors in the more phyric basalts. Although off-ridge features may have many values similar to N-MORB (normal MORB), MORB averages do not include these features, but data are included in the data file. Examples are Galapagos Rise, Walvis Ridge, and Rio Grande Rise.

An attempt has been made to give a designation for sample type when authors have made it easy to do so, but no attempt has been made to complete this information.

DISCUSSION

Aluminium Average Al_2O_3 in MORB goes along with average SiO_2. That is, the East Pacific Rise has the lowest average value (14.74%), the Mid-Atlantic Ridge is intermediate (15.98%), and the Indian Ocean Ridge system is the highest (16.18%). OIB seems to average distinctively less Al_2O_3 at 13.41% (Fitton et al., 1991), and herein Hawaii is found to average 12.60% and the Marquesas 13.07% at Mg #'s similar to MORB.

Barium Ba is a defining element for so-called normal MORB or N-MORB. MORB averages less than 100 ppm (average obtained is 50 ppm), with the East Pacific Rise averaging 33 ppm, the Mid-Atlantic Ridge 61 ppm, and the Indian Ocean Ridge system 51 ppm. Ba also is one of the elements thought to be susceptible to submarine weathering enrichment; however, it is noted that the Indian Ocean value is somewhat less than that for the Mid-Atlantic Ridge. In contrast, OIB averages 518 ppm Ba (Fitton et al., 1991) with Hawaiian Islands at 316 ppm and the Marquesas at 380 ppm. Even the Ba average for the Rio Grande Rise is very distinctive from N-MORB at 170 ppm. Ba can be concentrated in phlogopite and hornblende in the source.

Calcium Average MORB varies little in CaO content with the East Pacific Rise being somewhat the lowest (11.31%), the Mid-Atlantic Ridge intermediate (11.45%), and the Indian Ocean Ridge system the highest (11.67%). OIB averages distinctly lower CaO contents (10.37% (Fitton et al., 1991)), and herein is found to average 10.61% in Hawaii and 9.75% for the Marquesas.

Cerium The only rare earth element tabulated is Ce, and the data set is spotty; yet, the average MORB at 16 ppm is highly distinctive from OIB at similar Mg #'s. Average OIB is 102 ppm Ce (Fitton et al., 1991). Herein, Hawaii is found to average 67 ppm and the Marquesas 55 ppm. The Rio Grande Rise at 36 ppm Ce is also high compared to MORB.

Chromium The highest average Cr content is in MORB of the Mid-Atlantic Ridge (299 ppm), reflecting a higher Mg content than the East

Pacific Rise (224) and Indian Ocean (241) ridge systems. Average OIB has the highest Cr content (324 ppm (Fitton et al., 1991)). Hawaii averages 496 ppm Cr and the Marquesas 402 ppm.

<u>Copper</u> The average value for Cu in MORB is 70 ppm with no significant difference amongst the principal oceans, a value somewhat lower than the average for Zn. The range for the Pacific and Atlantic Oceans is 40-100 ppm; however, Cu contents in MORB from the Indian Ocean can be substantially higher than 100 ppm. The average value for the Indian Ocean, however, is similar to the other oceans because of many low values. This increased dispersion may reflect, in part, Cu redistribution during either submarine weathering or hydrothermal activity. A number of low Cu values, also, are due to inclusion of data on gabbros and anorthosites in the paper by Engel and Fisher (1975), but the Cu data by Klein et al. (1991) also appear to be uniformly low. OIB averaging 62 ppm (Fitton et al., 1991) are somewhat lower in Cu than MORB, although Hawaii is found to average 97 ppm Cu and the Marquesas 61 ppm. The Rio Grande Rise has an exceptionally high average for Cu of 192 ppm, which might be related to submarine alteration. Cu does not readily enter any of the common silicates; however, it can be >1% in any sulfides separating (Czamanske and Moore, 1977; Morgan and Baedecker, 1983). Cu seems to be easily reworked in submarine weathering and may appear as native Cu; it also is easily mobilized by hydrothermal activity.

<u>Iron</u> The average Fe content, expressed as Fe_2O_3, is highest for the East Pacific Rise (11.61%), with the Mid-Atlantic Ridge being intermediate (10.39%), and the Indian Ocean Ridge system the lowest (9.79%). Average OIB is substantially higher than MORB at 13.04% (Fitton et al., 1991). Hawaii has a similar average at 13.10% and the Marquesas somewhat less at 12.72%. The Rio Grande Rise is exceptionally high at 14.37%. Fe, particularly ferrous Fe, is thought to be very sensitive to submarine weathering, particularly oxidation.

<u>Magnesium</u> The East Pacific Rise has the lowest average MgO content (7.11%) and Mg # (57.24) compared to the Indian Ocean Ridge system (7.43%) and Mg # (62.30) and Mid-Atlantic Ridge (8.05%) and Mg # (62.77). Although OIB averages higher MgO (9.02% (Fitton et al., 1991)) than MORB, Fe is also higher in OIB so the Mg # at 60.35 is similar to MORB. Hawaii averages 10.17% MgO whereas the Marquesas average 8.56% still higher than for MORB. In this study, 10% of the total Fe is assumed to be ferric Fe in calculating Mg #'s (see <u>iron</u> for definition of Mg #). Some data on MORB glasses, however, suggest that 15% might be a better average, and this percentage is also commonly used in the literature.

<u>Manganese</u> Although frequently discussed in the literature, MnO is not very distinctive, found herein to average 0.17% in MORB and 0.18% in OIB (Fitton et al., 1991). Mn is concentrated in garnet, which may be a component in the source.

<u>Nickel</u> The average Ni content of MORB follows the Mg content.

Thus the Mid-Atlantic Ridge has the highest Ni content (128 ppm), Indian Ocean Ridge system in the middle (108 ppm), and the East Pacific Rise the lowest (82 ppm). OIB has the highest average Ni content (190 ppm (Fitton et al., 1991)) reflecting the higher Mg content. A prime repository of Ni is olivine; however, Ni also can be highly enriched in any sulfides separating (>1%)(Czamanske and Moore, 1977; Morgan and Baedecker, 1983).

Phosphorous P_2O_5 is very distinctive for MORB (0.18%) from OIB (0.68%), especially at similar values of Mg #. Hawaii averages 0.43% and the Marquesas 0.56% P_2O_5, although the Rio Grande Rise at 0.22% is only somewhat high for MORB.

Potassium The low level of K_2O (0.30%) is one of the defining elements for MORB and also is an element sensitive to submarine weathering. Some, in fact, use K_2O contents >0.30% to indicate alteration. The least altered basalts come from the East Pacific Rise (0.18%), and MORB from the Mid-Atlantic Ridge (0.22%) and Indian Ocean Ridge system (0.47%) contain more ferric Fe and H_2O, also taken to be signs of alteration. On the other hand, some make a special classification for the Indian Ocean and call them I-MORB. For comparison, however, OIB contains 1.24% K_2O on average and Hawaiian volcanic rocks 0.73%, so K_2O remains highly distinctive for MORB from OIB basalts, although the Rio Grande Rise is only somewhat high at 0.35%.

Silica The average SiO_2 content of East Pacific Rise MORB (50.08%) is somewhat less than for the Mid-Atlantic Ridge (50.13%) and Indian Ocean Ridge system (50.94%). The average SiO_2 content of OIB (Fitton et al., 1991) at 44.84% is substantially less than average MORB values.

Scandium Although the data set for Sc is spotty, Sc averages higher in MORB (herein found to be 37 ppm) than in OIB (23 ppm (Fitton et al., 1991)) at similar Mg #'s. Sc is thought to be enriched in clinopyroxine where the partition coefficient may be as large as four (Furman et al., 1991), but clinopyroxene is often rare or absent in MORB. None the less, most MORB differentiation models suggest important clinopyroxene differentiation. Sc can also be concentrated in magnetite, also rare in MORB, where the partition coefficient may be as high as three (Furman et al., 1991). Sc may be concentrated in garnet in the source of the melt.

Sodium Although the Na_2O content of MORB is thought to be sensitive to submarine weathering, the average Na_2O content varies little. The East Pacific Rise averages 2.66%, the Mid-Atlantic Ridge 2.71%, and the Indian Ocean Ridge System 2.50%. By and large the East Pacific Rise has the youngest, glassiest basalts that should be least affected by submarine weathering; yet it's average is in the middle. Furthermore, OIB averages only somewhat higher at 2.99%.

Strontium Sr (averaging 147 ppm) is also one of the defining elements of MORB, like K_2O and Ba. The East Pacific Rise averages 129 ppm Sr, the Mid-Atlantic Ridge 142 ppm, and the Indian Ocean Ridge system 167 ppm. OIB, however, averages 769 ppm Sr (Fitton et al., 1991), with Hawaii found herein to average 563 ppm and the Marquesas at 642 ppm. Sr is also sensitive to submarine weathering alteration and the high values for the Rio Grande Rise (348 ppm) may be problematical. In glassy MORB, however, Sr values above 200 ppm would be considered indicative of enriched or plume MORB (E-MORB or P-MORB).

Titanium TiO_2 has long been considered to be characteristic of MORB; however, it can vary substantially. Like Fe, TiO_2 is the highest in MORB of the East Pacific Rise (1.72%), intermediate in the Mid-Atlantic Ridge (1.43%), and lowest in the Indian Ocean Ridge system (1.31%). TiO_2 is thought to be immobile in submarine weathering. Thus the low TiO_2 content of Indian Ocean Ridge system MORB is probably a primary characteristic. It also suggests that the Fe averages are also approximately correct. High average TiO_2 (3.08%) is a characteristic of OIB (Fitton et al., 1991).

Vanadium Although V is usually thought to follow Fe and be highly enriched in oxides such as magnetite which has a partition coefficient >10 (Furman et al., 1991), the V content of Atlantic and Indian Ocean MORB is only marginally lower at 257 ppm than the higher Fe content volcanic rocks of OIB (275 ppm (Fitton et al., 1991). The East Pacific Rise basalts contain the highest average V content at 323 ppm. Like Sc, V is thought to be concentrated by clinopyroxene but with a partition coefficient closer to one (Furman et al., 1991).

Zinc The average Zn content of Mid-Ocean Ridge Basalts (MORB) is 84 ppm with a range of 40-140 ppm. The East Pacific Rise that averages 92 ppm Zn is somewhat greater than the values for the Atlantic (78 ppm) or Indian (82 ppm) oceans, reflecting the higher values for Fe and Ti along the East Pacific Rise. Average oceanic island basalts (OIB) at 115 ppm (Fitton et al., 1991) is higher than the average for MORB; however, MORB can average such values at individual localities (e.g., Southern Juan de Fuca Ridge at 120 ppm). The partition coefficient for Zn between olivine and melt is slightly larger than one (Gunn, 1971), around one-half for clinopyroxene and ilmenite, and perhaps >10 for titanomagnetite (Doe, 1994). Zn seems to be relatively insensitive to submarine weathering; however, it is very soluble in hydrothermal Cl-rich solutions.

Zirconium The average Zr content of East Pacific Rise (132 ppm) and Mid-Atlantic Ridge (130 ppm) MORB is similar; however, the Indian Ocean Ridge system averages substantially lower Zr (105 ppm). Zr, like Ti, is thought to be insensitive to submarine weathering.

COMBINATIONS

V/Zn On average, V/Zn is remarkably constant in MORB. For the East Pacific Rise it is 3.56 and 3.57 for both the Mid-Atlantic Ridge and Indian Ocean Ridge system; yet, the ratio on average is considerably less in OIB (2.39). Of the OIB or mixed localities considered herein, only the Rio Grande Rise (3.42) comes close to MORB, but the Rio Grande Rise has a much lower Mg #.

APPENDIX

<u>Incompatible nature of Zn</u> Clague et al. (1981) mention the incompatibility of Zn in oceanic basalts of the Galapagos Rise area so long as titanomagnetite does not separate. When titanomagnetite does separate significantly (which they observed at low Mg #'s), Zn becomes compatible. The incompatible nature of Zn is ascribed to clinopyroxene separation. Dissanayake and Vincent (1972) described Zn as increasing with differentiation in the Skaergaard intrusion of Greenland, i.e., Zn is incompatible. le Roex et al. (1992) show Zn to increase slightly with increase in Zr (a highly incompatible element) on their Fig. 4, but without comment on the text. Thus Zn appears to be slightly more incompatible than Zr (but less so than V which increases faster). As some Zn fits into clinopyroxene, but Zr does not (?), such behavior is surprising. In contrast, Sc decreases slightly with increase in Zr which would go with clinopyroxene separation. Widom et al. (1992) describe Zn as behaving incompatibly in the differentiation of trachytes in the Azores. Undiscussed data on Zn for Iceland in Furman et al. (1991) show Zn to behave slightly incompatibly although modeling by the authors includes substantial portions of magnetite among the phases to have differentiated. Thus depletion of Zn from magnetite separation may not be adequate to counteract the increase of Zn in the melt from separation of plagioclase and clinopyroxene.

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