Chemical Mass Balance of the Earth's Crust: The Calcium Dilemma (?) and the Role of Pelagic Sediments

Abstract. *Chemical mass balance between igneous and sedimentary rocks is calculated by using a linear least squares method in which all chemical variables are evaluated simultaneously. Previous estimates of the average chemical composition of sedimentary rocks have shown excess calcium because of failure to accurately represent the composition and mass of pelagic sediments.*

Fundamental to modeling the evolution of the earth's crust is the chemical mass balance between igneous rocks and sedimentary rocks. Previous studies (*1–4*) have approached this problem by combining the major igneous rock types (basalt, andesite, and granite) to form an average igneous rock. Weathering of this average igneous rock should yield an average sedimentary rock, which can be considered to be a combination of sandstone, shale, evaporite, and carbonate rocks. A common technique is to solve a set of simultaneous equations for the major elements in igneous and sedimentary rock types. A widely accepted solution to this set of equations is a combination of 40 percent granite, 40 percent andesite, and 20 percent basalt (or if only granite and basalt are used as the igneous parents, 66 percent granite and 33 percent basalt), which yields a sedimentary package composed of approximately 80 percent shale and nearly equal amounts of sandstone and carbonate rocks (*2, 3*). There are a number of disadvantages to this approach, the most serious being that the calculated abundances of sandstone, shale, and carbonate rocks do not correspond to estimates based on measured stratigraphic sections (*3*).

The difference between estimates based on measured stratigraphic sections and geochemical estimates is due to Ca excess in the measured sections. Ronov and Yaroshevsky (*5*), Garrels *et al.* (*6*), and Wolery and Sleep (*7*) recognized this Ca excess and suggested various means of accounting for it—mostly by some type of selective leaching of Ca from basic igneous rocks.

Our approach to the problem differs from others in two major respects. First, rather than initially selecting an average igneous rock, we chose an average sediment because there are more direct data on the composition of the average sediment. Second, we used a linear least squares computer method (*8, 9*) to solve the mixing equation.

The advantage of using the linear least squares method is that it uses all the available chemical data and evaluates how closely a parent rock may be expressed as a linear combination of individual rocks (components). The problem can be simply stated as a set of equations where the chemical composition of the parent rock is best approximated by the appropriate mixture of the components. The amount of each of the components needed to best match the parent is solved by a least squares technique, which minimizes the sum of the squares of the differences between the selected parent and the parent calculated by mixing the components. Acceptance of a particular model is based on the chemical composition of the calculated parent being within reasonable limits and the abundance of components (individual rocks) being similar to those that occur in nature.

Two average sediments, based on chemical analyses and relative proportions of sedimentary rocks, are those of Poldervaart (*10*) and Ronov (*11*). They differ in the estimated percentage of CaO by 5 percent, but are otherwise essentially the same. The major error in these average sediments is that they predate widespread recognition that the pelagic sediments presently on the sea floor were deposited only within the last 200 to 150 million years and that Paleozoic pelagic sediments must have contained much less CaO than present pelagic sediments because of the lack of calcareous plankton during the Paleozoic. Therefore, we have recalculated the average sediment by taking Ronov's (*11*) average continental sediment (platform and geosyncline) and adding to this our own estimate of relative volume and chemical composition of pelagic sediments. The volume is estimated by multiplying the area of pelagic sedimentation (268×10^6 km^2) by the product of the sedimentation rate (1 to 3 m per 10^6 years) and the length of time (1.5×10^9 years). (The volume of possible continental accretion does not significantly affect these numbers.) The sedimentation rate is that for pelagic red clays (*12, 13*) and the length of time (1.5 billion years) is from Ronov (*11*) since it represents his estimate of the time span over which the continental sediments he considered were deposited. The volume of pelagic sediments will vary between 44 and 71 percent of Ronov's calculated volume, depending on the sedimentation rate. We used 50 percent as a conservative estimate. Average sediments were also calculated on the assumption that pelagics make up 30 and 70 percent of the total sediments. Both these hypotheses were tested and rejected because negative proportions of components were generated. Sandstone, for instance, must be subtracted from the average sediment when we assume 30 percent pelagics. Therefore, an average sediment based on 50 percent pelagics, while not unique, is probably a reasonable choice.

The chemical composition of pelagic sediments used in this average sediment should be essentially the composition of Paleozoic and older pelagics because most of the continental sediments considered are pre-Mesozoic or derived from pre-Mesozoic sediments. Since most Paleozoic pelagic sediments must have been lost through subduction (*14*), we estimated their composition from El Wakeel and Riley's (*15*) average pelagic sediment calculated on a carbonate-, water-, and organic-free basis. The lack of carbonate in the Paleozoic is the significant difference between ancient and younger (last 150 million years) pelagic sediment (*16*).

There are few data on the volume and composition of metasediments younger than 1.5 billion years. Stratified metasediments and volcanics are estimated to be approximately 2 percent of the total sediments in the Appalachian Basin (*17*). If the volume of metasediments is 20 percent that of the total sediments and the composition is the average composition for the Canadian Shield, the calculated average sediment will not change significantly. Calcium oxide, for instance, will only change from 5.8 to 5.6 percent.

On the basis of these considerations, we calculated the average sediment shown in column 6 of Table 1. The suitability of this choice can be tested by using the least squares approximation method to determine if the linear combination of the chemical compositions of sandstone, shale, carbonate, evaporite, and pelagic rocks (components) yield this average sedimentary rock (parent). If the results are consistent, the test will result in reasonable residuals (differences between calculated and observed values of the average sediment) for the oxides; the sum of the squares of the residuals will be small, indicating a good overall fit; and the relative proportions of the five sedimentary rocks will be reasonable. The results are shown in Table 1. The largest residual is for K_2O and is within 10 percent of the observed value. All residuals are quite small, and the sum of the squares of the residuals indicates excellent overall agreement. A major advantage of this approach is that this is an independent test for internal consistency for the selection of an average sedimentary rock and is in no way based on any assumption about the composition of the igneous rocks from which it was ultimately derived.

Having defined an average sedimentary rock, we next examined models for the breakdown of igneous rocks to form it. An acceptable model is one in which the difference between the calculated and observed amount of an element or oxide is small (expressed as a percentage of the observed value). A further constraint is that the variable coefficient for all components except seawater must be positive. A positive variable coefficient for seawater would indicate that it is a primary source of oxides for sedimentary rocks, whereas a negative one would indicate that the igneous rocks break down to yield sediments plus seawater. Therefore, a test can be accepted only if the variable coefficient for seawater is negative.

A reasonable model to test is one in which tholeiitic basalt, an average continental crust [here taken to be the average chemical composition of the Canadian Shield (*18*)], seawater, and CO_2 are used as components to yield the average sedimentary rock. The results of this test are shown in Table 2. The largest residuals with respect to observed values are for Al_2O_3 and K_2O. The residuals for all other oxides are low, and the overall fit of the data is good.

Table 1. Linear least squares test for mixing the major sedimentary rocks (columns 1 to 5) to yield the estimated average sediment (column 6). Column 7 is the estimated average sediment calculated by the least squares approximation. Reference numbers for data sources are given in parentheses; the average evaporite composition was calculated from data in Ronov and Migdisov (*26*). The sum of squares of residuals is 0.12.

Oxide	Amount (percent by weight) in						
	1 Average evaporite	2 Average sandstone (*23*)	3 Average carbonate (*24*)	4 Average shale (*25*)	5 Average pelagic (*15*)	6 Average sedimentary rock	7 Least squares estimate of average sedimentary rock
SiO_2	0.0	77.6	8.2	58.1	61.5	55.6	55.6
Al_2O_3	0.0	7.1	2.2	15.4	18.1	15.5	15.4
Fe	0.0	2.4	1.2	4.6	6.4	5.3	5.3
MgO	0.0	1.2	7.7	2.4	3.2	3.2	3.4
CaO	15.0	3.1	40.5	3.1	1.0	5.8	5.7
Na_2O	23.9	1.2	0.0	1.3	2.0	1.8	1.9
K_2O	1.1	1.3	0.0	3.2	3.2	2.6	2.8
CO_2	0.0	2.5	35.5	2.6	0.0	4.1	4.2
	Calculated proportions						
	0.01	0.03	0.10	0.21	0.64		

Table 2. Linear least squares test for mixing the average continental rock (column 1), tholeiitic basalt (column 2), CO_2, and seawater to yield the average sediment. Column 6 is the estimated average sediment calculated by the least squares approximation. The sum of squares of residuals is 1.91.

Oxide	Amount (percent by weight) in					
	1 Average continental rock (*18*)	2 Average tholeiite (*27*)	3 CO_2	4 Seawater	5 Average sedimentary rock	6 Least squares estimate of average sedimentary rock
SiO_2	64.9	51.1	0.0	0.00	55.6	55.8
Al_2O_3	14.6	16.2	0.0	0.00	15.5	14.5
Fe	3.1	8.3	0.0	0.00	5.3	5.1
MgO	2.2	6.2	0.0	0.20	3.2	3.6
CaO	4.1	9.9	0.0	0.06	5.8	6.2
Na_2O	3.4	2.5	0.0	1.40	1.8	1.7
K_2O	3.1	0.7	0.0	0.05	2.6	1.9
CO_2	0.0	0.0	1.0	0.01	4.1	4.1
	Calculated proportions					
	0.53	0.41	4.11	−0.79		

The most important point demonstrated by the data in Table 2 is that there is no significant Ca excess. It appears to us that the Ca dilemma is the result of failure to take into account both abundance and composition of Paleozoic pelagic sediments.

The results of this study point out the need to evaluate the effect of changes in the composition of pelagic sediments in subduction zones. Pelagic sediments, in contrast to other sediments, are not usually recycled; most are subducted and therefore act as a geochemical sink (*19*). Models for the chemical evolution of the earth's crust may need to take into account the fact that vast amounts of pelagic material are subducted and that the chemistry of these pelagics changes with time. The major change in the last 150 million years is that calcite has become a major mineral in pelagic sediments. Wyllie and Huang (*20*), Eggler (*21*), and Mysen (*22*) have shown that partial melts produced in the mantle are strongly influenced by the presence of CO_2 and therefore, as carbonate becomes abundant in pelagic sediments, there should be a corresponding change in the composition of mantle melts produced above subduction zones.

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20 October 1975; revised 27 February 1976

Fly Ash Collected from Electrostatic Precipitators: Microcrystalline Structures and the Mystery of the Spheres

Abstract. *Scanning electron micrographs demonstrate the presence of microcrystalline structures on the surface of coal-derived fly ash samples taken from electrostatic precipitator hoppers. Cenospheres (hollow spheres) were found to be packed with smaller cenospheres, which were also packed with spheres. Microspheres, apparently formed by uneven heating, are encapsulated in the parent sphere. Chemical analyses provide a basis for the postulation of a mechanism of formation for plerospheres (hollow spheres packed with spheres) and microcrystals.*

Elucidation of the potential bioenvironmental effects of various options for the generation of electric power necessitates a physicochemical and biological evaluation of agents released to the environment. As part of our initial efforts to characterize fossil fuel–derived effluents, a detailed investigation of the physical appearance of fly ash was carried out by scanning electron microscopy (SEM). This report describes our findings of microcrystalline structures and cenospheres (hollow spheres) packed with smaller spheres in fly ash collected from electrostatic precipitators (ESP) in coal-fired power plants.

Fly ash samples from two coal-fired power plants, one burning a coal with a low sulfur content (western U.S. coal) and the other burning a coal with a high sulfur content (eastern U.S. coal) were obtained from ESP hoppers. Two fly ash samples from western U.S. coal were collected: one from a hopper at ambient temperatures 30 days after the boiler had been shut down and the second sample from a hopper at about 66°C while the generating unit was in operation. The fly ash sample from eastern U.S. coal was collected from an ESP operating at 125°C.

Fly ash agglomerate composed of spherical particles, shown in the SEM micrograph (Fig. 1A), has been described by a number of investigators as being typical of fly ash derived from coal combustion (*1*). The cenospheres of Fig. 1B are, however, more typical of the particulate aggregates that we have collected. Careful examination of these cenospheres reveals that some of the larger spheres contained within a cenosphere are themselves cenospheres packed with smaller spheres 1 μm in diameter or less. Microcrystals can also be observed on the surface of the large cenosphere as well as on the smaller entrapped spheres. At higher magnification (Fig. 1B, inset) the microcrystals appear to be growing from the surface of the spheres. High local concentrations of crystals (Fig. 1C) could be found in the fly ash sample from western U.S. coal from the generating unit that had been shut down. Although the fly ash from western U.S. coal collected at 66°C also contained a large number of cenospheres with packed spheres (Fig. 1D), microcrystals were not evident. However, in the fly ash agglomerate of Fig. 1E, the lower particle shows a striated surface apparently resulting from initial crystal formation. Spherical cavities in the thick wall of the upper hollow particle were either gas pockets or the remnants of smaller encapsulated spheres. The micrographs in Fig. 1, D and E, were prepared within 2 weeks after collection of the fly ash from western U.S. coal. Subsequent SEM analysis of the fly ash collected at 66°C after it had been stored in closed containers at ambient temperatures for 4 months revealed extensive crystal growth on the surface of the spheres, an indication that the crystal formation occurs gradually after the spherical particles have developed.

The fly ash from eastern U.S. coal contained a larger fraction of amorphous material than that from western U.S. coal, although both contained cenospheres. A typical fly ash aggregate from eastern U.S. coal (Fig. 1F) is composed of spherical particles embedded in an amorphous matrix.

Using light microscopy, we observed unbroken spheres with a "cloudy" interior, as described by McCrone *et al.* (*2*); we found that we could "crack" the spheres by compressing them between two microscope slides and that smaller spheres were contained in the larger spheres. As these spheres are not empty, we suggest that the name "plerosphere" [plero- (from the Greek *plērēs*, full)] be applied to these hollow spheres packed with spheres.

The empirical formula of the major elements in the fly ash from western U.S. coal analyzed by atomic absorption spectroscopy is $Si_{1.00}Al_{0.45}Ca_{0.051}Na_{0.047}Fe_{0.039}Mg_{0.020}K_{0.017}Ti_{0.011}$. When expressed as the associated oxides, the elements are present in the following mass percentages: SiO_2, 65.3; Al_2O_3, 25.2; Fe_2O_3, 3.4; CaO, 3.1; Na_2O, 1.6; TiO_2, 0.98; MgO, 0.89; and K_2O, 0.89. This chemical composition is consistent with fly ash originating from coal with intrusions of clay minerals, probably kaolinite minerals with lesser amounts of quartz (*3*). As calcium does not occur within the lattice structure of these minerals, the calcium present in the fly ash was probably derived from intrusions of calcium carbonate. Electron microprobe analysis of the plerospheres indicated that the surface was predominantly aluminosilicate glass, with intermediate concentrations of iron, calcium, sodium, and magnesium, and minor concentrations of titanium and sulfur. Inclusions with higher concentrations of calcium were found within the surfaces; smaller particles were found in which titanium or iron were the only elements detected. Microprobe analysis of larger crystals (20 μm in length) with a physical appearance similar to those of Fig. 1C indicated high concentrations of calcium and sulfur with no other elements detected. The limits of detectability for other elements in these particles by electron-probe analysis are on the order of 0.1 percent (*4*). The major gases contained within the spheres were H_2O and CO_2 (*5*), as determined by mass spectroscopic analysis after thorough removal of surface-associated gases and repeated crushing of the spheres in a vacuum.

The slow crystal formation process appears to involve the crystallization of soluble substances from liquid condensed on the particle surface. Moreover, the microprobe analysis and the SEM appearance of the larger crystals indicate that these larger crystals are probably anhydrite ($CaSO_4$) or gypsum ($CaSO_4 \cdot 2H_2O$) (*6*). Thus the microcrystals are probably formed by the leaching of metal oxides by condensed