Barium 56

A	K. Fischer	(Lehrstuhl für Kristallographie, Universität des Saarlandes, Saarbrücken, Germany)
B—O	H. Puchelt	(Mineralogisch-Petrographisches Institut der Universität, Tübingen, Germany)

56-A. Crystal Chemistry

I. General

In the crystal structures of barium minerals, Ba is surrounded by O, OH, H_2O or a halogen ion as nearest neighbors. Its valency is two and the bond type is predominantly ionic. Of the divalent positive ions, Ba^{2+} has the largest ionic radius (except Ra^{2+}). Isostructural replacement of, or by, other large cations such as Pb^{2+} and Sr^{2+} is frequently observed. Less common is replacement of K^+ and of the smaller ion Ca^{2+}. A few examples of crystal chemical relations which are not listed in the tables below are the following synthetic compounds: $BaFe_{12}O_{19}$, $BaAl_{12}O_{19}$, $SrFe_{12}O_{19}$, $SrAl_{12}O_{19}$ etc. in the magnetoplumbite series; pandaite with Ba partially replacing Ca in the pyrochlore group; isotypy of $K[NO_3]$ and witherite $Ba[CO_3]$; Ca—Ba-mimetisite; heinrichite and meta-uranocircite in the torbernite and meta-torbernite group.

The coordination of Ba has been reviewed by MANOHAR and RAMASESHAN (1964). The coordination number ranges from 6 to 12 for O, OH, H_2O. The existence of a large variety of coordination polyhedra is illustrated in Tables 51-A-1, 51-A-2, and 51-A-3 in which crystal structures of Ba minerals and a few selected synthetic compounds are listed. In general, oxygen atoms with distances larger than 3.3 Å are not considered as sharing one coordination polyhedron (exception: barite). This limitation appears to be justified as in the majority of the structures the distance of the "next-nearest" O neighbors is substantially larger than the range of distances attributed to the first-order coordination. In other cases, however, the distances show a broad and rather uniform range of variation (e.g. Ba_3 in taramellite) so that it is difficult to define the coordination number. The type of coordination polyhedron of Ba apparently has a minor influence on the energy balance of these structures. Nevertheless it can control the structure type as has been demonstrated for silicates by LIEBAU (1962, 1968).

The following averages for atomic distances were obtained for the different coordination numbers indicated:

Coordination number	Atomic distance, Å	
6	2.7_6	(BaO, $BaZnO_2$, benitoite)
7	2.7_8	(paracelsian, $Ba[GeO_3]$ high)
8	2.8_1	($BaNiO_2$, $Ba(OH)_2 \cdot 8H_2O$, $BaUO_4$, gillespite, taramellite)
9	2.8_5	($Ba[S_2O_6] \cdot 2H_2O$, $Ba[B(OH)_4]_2$, $Ba[B_4O_7]$, celsian, sanbornite)
10	2.8_7	(BaO_2, $BaTi_4O_9$, $Ba[B_4O_7]$, $Ba_3[PO_4]_2$)
12	2.9_3	(psilomelane, high $BaTiO_3$, nitrobarite, barite, norsethite, $Ba_3[PO_4]_2$, "hexagonal" $Ba[Al_2Si_2O_8]$, α-$BaO_2 \cdot 2H_2O_2$)

These data demonstrate a general increase of distance with increasing coordination number. This can be considered only as a first approximation because of the restricted selection of minerals and artificial compounds; (for some other compounds used for the computation of the averages, which are not listed in Tables 56-A-1, 56-A-2 and 56-A-3, see MANOHAR and RAMASESHAN, 1964).

II. Crystal Chemistry of Some Minerals and Synthetic Compounds

a) Oxides, Halides

The structure of psilomelane $(Ba, H_2O)_2Mn_5O_{10}$ consists of MnO_6 octahedra and $(Ba, H_2O)O_{12}$ cubo-octahedra (only oxygen atoms with distances ≤ 3.16 Å are considered). Ba and H_2O occupy the same equipoint (partial ordering assumed), probably because of very similar distances of Ba—O and O—H_2O atoms and molecules (H-bridges?). The crystal structure of hollandite $BaMn_8O_{16}$ has the same coordination polyhedron for Ba (BYSTRÖM and BYSTRÖM, SR 13, 1950, 186). In synthetic oxides and hydroxides almost all coordination numbers from 6 to 12 occur;

Table 56-A-1. *Coordination of Ba in some oxides and halides*

Mineral or synthetic compound	Coordinated atoms, distances to Ba in Å		Coordination polyhedron	References
$Ba^{[6]}O^{[6]}$	6O	2.76	octahedron	1
$Ba^{[6]}Zn^{[4]}O_2$	6O (2O	2.64—2.97 3.36)	octahedron, severely distorted	2
$Ba^{[8]}Ni^{[4]}O_2$	8O	2.80; 2.84	quadratic prism, severely distorted	3
$Ba^{[8]}(OH)_2 \cdot 8H_2O$	8OH	2.69—2.77	distorted quadratic antiprism	4
$Ba^{[8]}U^{[6]}O_4$	8O	2.71—2.99	irregular	5
$Ba^{[10]}O_2$	8O 2O	2.79 2.68	tetragonal prism with tetragonal pyramids on two base faces	6
$Ba^{[10]}Ti_4^{[6]}O_9$	10O	2.81—3.09	pentagonal prism	7
psilomelane, $(Ba, H_2O)_2^{[12]}Mn_5^{[6]}O^{10}$	8O $4H_2O$	2.85—3.16 2.78; 2.88	distorted cubo-octahedron	8
$Ba^{[12]}Ti^{[6]}O_3$ (high-temp. phase)	12O	2.83	cubo-octahedron	9
$Ba^{[8]}F_2^{[4]}$	8F	2.68	cube	10
$Ba^{[9]}Cl_2 \cdot 2H_2O$	7Cl $2H_2O$	3.14—3.38 2.76	distorted trigonal prism with 2Cl and $1H_2O$ on top of prismatic faces	11

References: 1. GERLACH (SB 1913—1928, 119). 2. v. SCHNERING, HOPPE and ZEMANN (SR 24, 1960, 454). 3. LANDER (SR 15, 1951, 180); for structure, see LANDER (1951). 4. MANOHAR and RAMASESHAN (1964). 5. SAMSON and SILLÉN (SR 11, 1947—48, 441). 6. ABRAHAMS and KALNAJS (SR 18, 1954, 364). 7. TEMPLETON and DAUBEN (SR 24, 1960, 326). 8. WADSLEY (SR 17, 1953, 429). 9. GOLDSCHMIDT (SB 1, 1913—1928, 333). 10. DAVEY (SB 1, 1913—1928, 187). 11. JENSEN (SR 10, 1945—1946, 95).

halides and hydrated halides are known with coordination numbers of 8 and 9. A selection of these compounds (especially oxides and hydroxides with coordination polyhedrons not described for minerals in this section) is included in Table 56-A-1.

b) Nitrates, Carbonates, Borates

The BaO_{12} icosahedron found in nitrobarite $Ba[NO_3]_2$ was also observed in $Ba[ClO_4]_2 \cdot 3H_2O$, α-$BaO_2 \cdot 2H_2O_2$, $Ba[SiF_6]$ and $Ba[GeF_6]$ (Manohar and Ramaseshan, 1964). In the carbonate minerals, Ba replaces Ca in the aragonite series (witherite and solid solutions) with a coordination polyhedron which can be described as a distorted cube with one of its edges elongated for housing the 9th O atom above its centre; the same coordination polyhedron is also reported for sanbornite $Ba_2[Si_4O_{10}]$. Barytocalcite $BaCa[CO_3]_2$ has an independent structure also with a coordination number of 9 (two distances of 3.28 and 3.30 Å are not included). In norsethite, $BaMg[CO_3]_2$, Ba has a $6+6$ coordination forming a distorted ditrigonal prism (Lippmann, 1968). No barium borate mineral structures are known at present. Of the synthetic borates, $Ba[B(OH)_4]_2$ is isostructural with the corresponding Sr borate (see subsection 38-A-II), whereas $Ba[B_4O_7]$ is not (coordination numbers 9 and 10).

c) Sulfates, Phosphates

Barite $Ba[SO_4]$ is isostructural with anglesite $Pb[SO_4]$ and celestite $Sr[SO_4]$. (Solid solutions are known as angleso-barite, baryto-celestite and calcio-barite.)

Table 56-A-2. *Coordination of Ba in some oxo-salts*

Mineral or synthetic compound	Coordinated atoms, distances to Ba in Å			Coordination polyhedron	References
Nitrobarite, $Ba^{[12]}[NO_3]_2$		$6+6$O	2.86; 2.95	distorted icosahedron	1
Witherite, $Ba^{[9]}[CO_3]$		9O	ca. 2.8	see text	2
Barytocalcite, $Ba^{[9]}Ca^{[6]}[CO_3]_2$		9O (2O	2.56—2.99 3.28; 3.30)		3
Norsethite, $Ba^{[12]}Mg^{[6]}[CO_3]_2$		$6+6$O	2.72; 3.18	distorted ditrigonal prism	4
$Ba^{[9]}[B(OH)_4]_2$	Ba_1:	9OH	2.73—2.90	trigonal prism with	5
	Ba_2:	9OH	2.77—2.99	centered faces	
$Ba^{[9]}Ba^{[10]}[B_4^{[3]}B_4^{[4]}O_{14}]$	Ba_1: Ba_2:	9O 10O	2.61—3.08 2.71—3.12	irregular	6
Barite, $Ba^{[12]}[SO_4]$		10O (2O	2.76—3.08 3.30)	see text	7
$Ba^{[12]}Ba_2^{[10]}[PO_4]_2$	Ba_1:	$6+6$O	2.80; 3.23	distorted icosahedron	8
	Ba_2:	10O	2.71—2.83	see text	

References: 1. Vegard and Bilberg (SB **2**, 1928—1932, 386); cf. Lutz (SR **24**, 1960, 421). 2. Colby and La Coste (SB **3**, 1933—35, 407). 3. Alm (SR **24**, 1960, 425). 4. Lippmann (1968). 5. Kravchenko (1965). Block and Perloff (1965). 7. Sahl (1963); see also Colville and Staudhammer (1967). 8. Zachariasen (SR **11**, 1947—48, 388).

The coordination polyhedron based on a coordination number of 12 consists of two nearly parallel rings of 5 and 6 oxygens on both sides of the Ba atom, with a 12th O on top of the 6-ring (for an alternative description, see Manohar and Ramaseshan, 1964). In this coordination polyhedron, 2 O with distances of 3.30 Å are included. Omitting them from the 5-ring would lead to a rather one-sided coordination polyhedron (Sahl, 1963). $Ba_3[PO_4]_2$, isostructural with $Sr_3[PO_4]_2$, has two coordination polyhedra for Ba with coordination numbers of 12 and 10; the latter one consists of a distorted "hexagonal" pyramid (symmetry $3m$) slightly above the Ba atom and a triangle below.

d) Silicates

$Ba_2^{[6]}[SiO_4]$ and $Sr_2^{[6]}[SiO_4]$ are isostructural with olivine (O'Daniel and Tscheischwili, SR 9, 1942—44, 261). Another silicate with isolated tetrahedra, $BaO \cdot SiO_2 \cdot 6H_2O$, has two different coordination polyhedra with coordination numbers of 8 and 10 which share faces with each other but have no common corner with the $[SiO_4]$ tetrahedron. The ten-fold coordination can be described as a pentagonal pyramid above a square. In benitoite $BaTi[Si_3O_9]$ (isomorphous to pabstite $BaSn[Si_3O_9]$), the coordination polyhedron is severely distorted. (The next 6 O atoms beyond the nearest ligands are not considered because of their distance of 3.43 Å.) Taramellite $Ba_2(Fe, Ti, Mg)_2[Si_4O_{12}](OH)_2$, with rings of $4[SiO_4]$ tetrahedra, has three different coordination polyhedra for Ba with a coordination number of 6, 6 and 7 (?). The last coordination polyhedron can also be described as having a coordination number of 9 (two additional O's at a distance of 3.12 Å) or with a coordination number of 11 (two additional oxygen atoms at a distance of 3.21 Å). $Ba[GeO_3]$, with a germanate chain of the "Zweierketten"-type, is one of the few examples for a coordination number of 7. (Higher condensed silicate chains with Ba as cations have been investigated by Katscher and Liebau (1965, 1966)). In the sheet silicates, small percentages of Ba have been found in some muscovites. The mineral anandite $(Ba, K)(Fe, Mg)_3[(Si, Al, Fe)_4O_{10}](O, OH)_2$ was recently described as a member of the trioctahedral mica family (Pattiaratchi, Saari and Sahama, 1967). Other Ba silicates with single sheet structures do not have the usual plane silicate sheet of the mica type and do not contain OH or H_2O (Liebau, 1968). Sanbornite, $Ba[Si_2O_5]$, with undulating sheets built of 6-membered rings has the same coordination polyhedron for a coordination number of 9 as described for witherite. In the structure of gillespite $BaFe[Si_4O_{10}]$ (with folded sheets of 4- and 8-membered rings of $[SiO_4]$ tetrahedra), the coordination polyhedron of Ba can be derived from a cube whose faces are each divided into 2 triangles to form a triangular dodecahedron of symmetry $\bar{4}$ (cf. also cuprorivaite: Pabst, 1959; Mazzi and Pabst, 1962). Ba replaces Sr or Ca in synthetic compounds of the melilite series ($Ba_2[Fe^{[4]}Si_2O_7]$, $Ba_2[Mn^{[4]}Si_2O_7]$, cf. Wyckoff, 1968, p. 225—227)[1]. For the non-feldspar form of $Ba[Al_2Si_2O_8]$, containing double sheets, a hexagonal (or pseudo-hexagonal) prism has been described as the coordination polyhedron (on the orthorhombic distortion, cf. Takéuchi, SR 22, 1958, 501). The same coordination polyhedron has been found in cymrite $Ba[AlSi_3O_8(OH)]$. In the Ba-feldspar celsian $Ba[Al_2Si_2O_8]$, the coordination polyhedron is similar to that in witherite (if a tenth oxygen atom at a

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[1] The classification of tetrahedral structures follows Zoltai's suggestion (1960).

Table 56-A-3. *Coordination of Ba in some silicates*

Mineral or synthetic compound	Coordinated atoms, distances to Ba in Å		Coordination polyhedron	Ref.
$BaO \cdot SiO_2 \cdot 6H_2O$	Ba_1: 8OH, H_2O	2.83—2.90	distorted quadratic antiprism	1
	Ba_2: 10OH, H_2O	2.83—2.90	see text	
Benitoite, $Ba^{[6]}Ti^{[6]}[Si_3O_9]$	6O	2.77	heavily distorted octahedron or trigonal prism	2
Taramellite, $Ba_2(Fe, Ti, Mg)_2^{[6]}(OH)_2[Si_4O_{12}]$	Ba_1: 6O	2.83; 2.90	distorted hexagon	3
	Ba_2: 6O	2.73; 2.75	distorted trigonal prism	
	Ba_3: 7O (2+2O	2.71—3.00 3.12; 3.21)	see text	
$^1_\infty Ba^{[7]}[Ge^{[4]}O_3]$ (high)	7O	2.62—2.94	irregular	4
Sanbornite, $^2_\infty Ba^{[9]}[Si_2O_5]$	7O 2O	2.74—2.94 3.14	see text	5
$^2_\infty$Gillespite, $Ba^{[8]}Fe^{[4pl]}[Si_4O_{10}]$	8O	2.73; 2.98	heavily distorted cube or trigonal dodecahedron	6
$Ba^{[12]}[Al_2Si_2O_8]$ ("hexagonal celsian")	12O	~2.89	hexagonal prism	7
Cymrite, $Ba^{[12]}[AlSi_3O_8(OH)]$	12O ($2 \times \frac{1}{2} H_2O$	3.05 3.39)	hexagonal prism	8
Celsian, $Ba^{[9]}[Al_2Si_2O_8]$	9O (1O	2.67—3.14 3.42)	see text	9
Paracelsian, $Ba^{[7]}[Al_2Si_2O_8]$	7O (2O	2.73—2.83 3.32; 3.37)	see text	10
Barylite, $Ba^{[12?]}[Be_2^{[4]}Si_2O_7]$	11O (1O	2.82—3.12 3.34)	distorted cubo-octahedron (minus one?)	11
Harmotome, $Ba^{[10]}[Al_2Si_6O_{16}] \cdot 6H_2O$	8O, H_2O 2O	2.77—3.08 3.26	see text	12

References: 1. Höhne and Dornberger-Schiff (SR 26, 1961, 513). 2. Fischer (1969). 3. Mazzi and Rossi (1965). 4. Hilmer (1962). 5. Douglass (SR 22, 1958, 490). 6. Pabst (SR 9, 1942—44, 249); cf. Mazzi and Pabst (1962), Pabst (SR 23, 1959, 486). 7. Matsumoto (SR 15, 1951, 304); cf. Takéuchi (SR 22, 1958, 501). 8. Kashaev (1966). 9. Newnham and Megaw (SR 24, 1960, 491). 10. Bakakin and Belov (SR 24, 1960, 492); cf. Smith (SR 17, 1953, 556). 11. Abrashew, Ilyukhin and Belov (1964). 12. Sadanaga, Marumo and Takéuchi (SR 26, 1961, 532).

distance of 3.42 Å is not counted), with one surprisingly short distance of 2.67 Å (see Newnham and Megaw, SR 24, 1960, 491). In the framework structure of paracelsian (with the same chemical composition as celsian), which has a structure closely related to danburite $Ca[B_2^{[4]}Si_2O_8]$, a similar coordination polyhedron with a coordination number of 9 has been described, including two distances larger than 3.3 Å. Omitting these latter two oxygen atoms, the coordination polyhedron consists of a distorted rectangle with Ba nearly in its plane plus two oxygen atoms forming a gable-roof on top of it and the seventh oxygen below its centre. The distorted cubo-octahedra around Ba in barylite $Ba[Be_2Si_2O_7]$ (with one distance larger than 3.3 Å), form chains by linked triangles. Two crystal structures of natural Ba-zeolites, edingtonite $Ba[Al_2Si_3O_{10}] \cdot 4H_2O$ (Taylor and Jackson, SB 3, 1933 to 1935, 529) and harmotome $Ba[Al_2Si_6O_{16}] \cdot 6H_2O$ are known. In harmotome, Ba is surrounded by ten O or H_2O in a coordination polyhedron similar to that of $BaO \cdot SiO_2 \cdot 6H_2O$. Two of the 6 distances from Ba to framework oxygen atoms are rather long (3.26 Å).

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56-B. Isotopes in Nature

Natural Ba is a mixture of seven stable isotopes (Table 56-B-1). The atomic weight is 137.34 (Atomic Weight Conference of the Iupac, 1961, Butterworth Scientific Publications, 1962), calculated on the basis that $^{12}C = 12.00000000$.

Table 56-B-1. *Stable Ba isotopes in nature*
(Strominger *et al.*, 1958; Mattauch *et al.*, 1965; Eugster *et al.*, 1969)

Stable isotopes	% in natural mixtures	Isotope masses $^{12}C = 12.00000000$
^{130}Ba	0.1056 ± 0.0002	129.9062
^{132}Ba	0.1012 ± 0.0002	131.9051
^{134}Ba	2.417 ± 0.003	133.9046
^{135}Ba	6.592 ± 0.002	134.9056
^{136}Ba	7.853 ± 0.004	135.9043
^{137}Ba	11.232 ± 0.004	136.9055
^{138}Ba	71.699 ± 0.007	137.9050

Measurements (I) made by Umemoto (1962) indicate an enrichment of the lighter Ba isotopes in the Pasamonte and Nuevo Laredo achondrites and Bruderheim chondrite with a maximum of 2.5% for ^{130}Ba in the Bruderheim achondrite. This potential accumulation decreases almost linearly to mass ^{138}Ba.

Recent investigations of Ba isotope distribution in meteorites (Eugster *et al.*, 1969) showed that differences in isotopic composition between meteoritic and terrestrial samples are always $< 0.1\%$ for all isotopes.

A very small amount of the short-lived ^{140}Ba occurs in nature as a fission product of ^{238}U (Kuroda and Edwards, 1957; Heydegger and Kuroda, 1959).

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56-C. Abundance in Cosmos, Meteorites, Tektites, and Lunar Samples

I. Cosmos

Ba has been detected spectroscopically in stars of all spectral classes except classes O and B. These classes correspond to such high temperatures that all resonance transitions of the highly ionized atoms fall into the ultraviolet range, which is inaccessible for terrestrial observation. Ba abundances are normally given as atomic ratios per 10^{12} H atoms or 10^{6} Si atoms, or as ratios of Ba atoms/Fe atoms.

Atmospheres of main sequence stars always seem to contain Ba in similar concentrations. In Table 56-C-1, the sun is given as one example. Pronounced differences of Ba concentrations have been reported for two other groups of stars which do not belong to the main sequence. Ba II stars, which are considered to be carbon stars with higher temperatures than N stars (Gordon, 1968), exhibit an overabundance of s process elements, including Ba (Bidelman and Keenan, 1951; Burbidge and Burbidge, 1957; Warner, 1965). Fujita and Tsuji (1965) found s process

Table 56-C-1. *Barium abundance in stars*

Type of star	Name	log Ba for log H = 12.00	Reference
High velocity stars:			
F 6 IV-V	γ Serpentis	2.09	Kegel (1962)
Subdwarf	HD 140283	0.11	Baschek (1962)
Horizontal branch	HD 161817	0.94	Kodaira (1964)
Subdwarf	HD 19445	0.35	Aller, Greenstein (1960)
Subdwarf	HD 122563	−2.65	Wallerstein, Parker, Greenstein, Helfer, Aller (1963)
Main sequence stars:			
G 2 V	sun	2.10	Goldberg *et al.* (1960)
Other stars			
G 8 III	ε Virginis	2.01	Cayrel, Cayrel (1966)
		$(\log \mathrm{Ba}/\log \mathrm{Fe})_{\mathrm{star}}$ $-(\log \mathrm{Ba}/\log \mathrm{Fe})_{\mathrm{sun}}$	
Main sequence stars:			
G V	β Com	0.06 ± 0.20	Helfer *et al.* (1963)
G V	99 Her A	0.11 ± 0.20	Helfer *et al.* (1963)
G V	85 Peg A	−0.10 ± 0.20	Helfer *et al.* (1963)
Other stars (subgiant):			
G IV	ζ Her	0.02 ± 0.15	Helfer *et al.* (1963)

elements in N star Y CVn to be overabundant by factors of 10^2 to 10^3 when compared to main sequence stars. Strong enhancement of Ba lines in N stars has been detected by Gordon (1968) and Utsumi (1967). A certain relationship of BaII stars to S type stars was observed (Warner, 1965) whereas R stars show normal Ba abundances. Clayton (1964) has developed the idea that in a special type of s process nucleosynthesis, the elements heavier than Zr are favored and this process is assumed to work in BaII stars.

Population II stars which are characterized by their high velocity show higher atomic ratios, H/Ba, than main sequence stars. Nevertheless, the abundance ratios of elements heavier than carbon are similar to main sequence stars (Unsöld, 1967). Burbidge and Burbidge (1957) found that the subdwarfs HD 106223 and λ Bootis are depleted in Ba by factors of 20 to 30.

Aller (1961) gives the logarithms of the ratio, number of Ba atoms in the sun/number of Ba atoms in the star, in the subdwarf for three typical subdwarfs: HD 140283, $\log(N_{sun}/N_{star}) = 2.59$; HD 19445, $\log(N_{sun}/N_{star}) = 2.15$; HD 219617, $\log(N_{sun}/N_{star}) = 1.40$. Spectral measurements for the CH stars HD 26 and HD 626 (Wallerstein and Greenstein, 1964) and comparison to the G 8III star ε Virginis showed them to be Ba deficient by a factor of 30 to 50. Helfer *et al.* (1963) gave the logarithms of atomic ratios $(N_{Ba}/N_{Fe})_{star} - (N_{Ba}/N_{Fe})_{sun}$ for four αG stars: ζ Herculis ($+0.02 \pm 0.15$), β Comae Berenicis ($+0.06 \pm 0.20$), 99 Herculis ($+0.11 \pm 0.20$), 85 Pegasi (-0.10 ± 0.20). Logarithms of atomic abundances of Ba in cosmos are published by Allen (1963) as 2.11 for $H = 12$. The weight ratio is 4.25. Suess and Urey (1956) and Cameron (1959) calculated the ratio of Ba atoms per 10^6 Si atoms as 3.66; in the sun the same ratio is 3.978 (Aller, 1961).

II. Meteorites

The published data are summarized in Tables 56-C-2 and 3. Distribution patterns of Ba are plotted in Figures 56-C-1a through d. Generally meteorite "finds" show higher Ba values than "falls", indicating a probable terrestrial contamination of the "finds". Thus a log of the normal distribution of Ba can be observed only in chondrite falls, whereas the "finds" of the same class exhibit a random distribution.

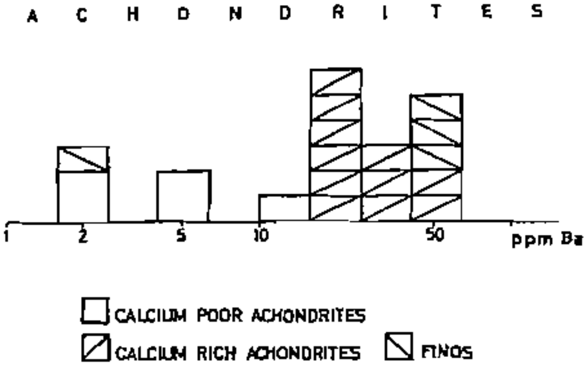

Fig. 56-C-1a. Distribution of Barium in achondrites

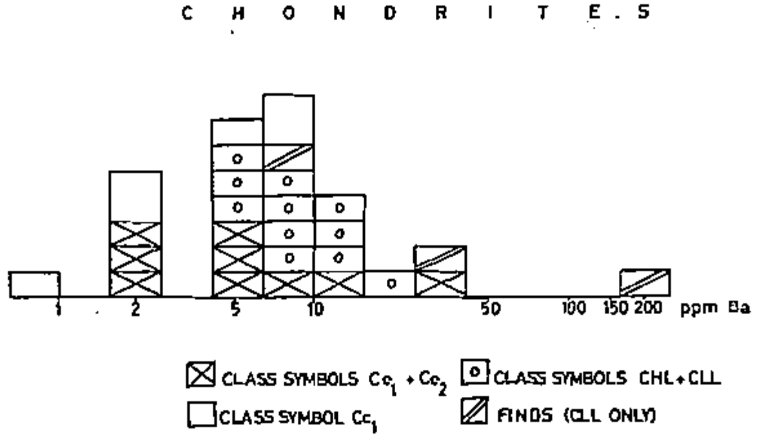

Fig. 56-C-1b. Distribution of Barium in carbonaceous and enstatite chondrites etc.

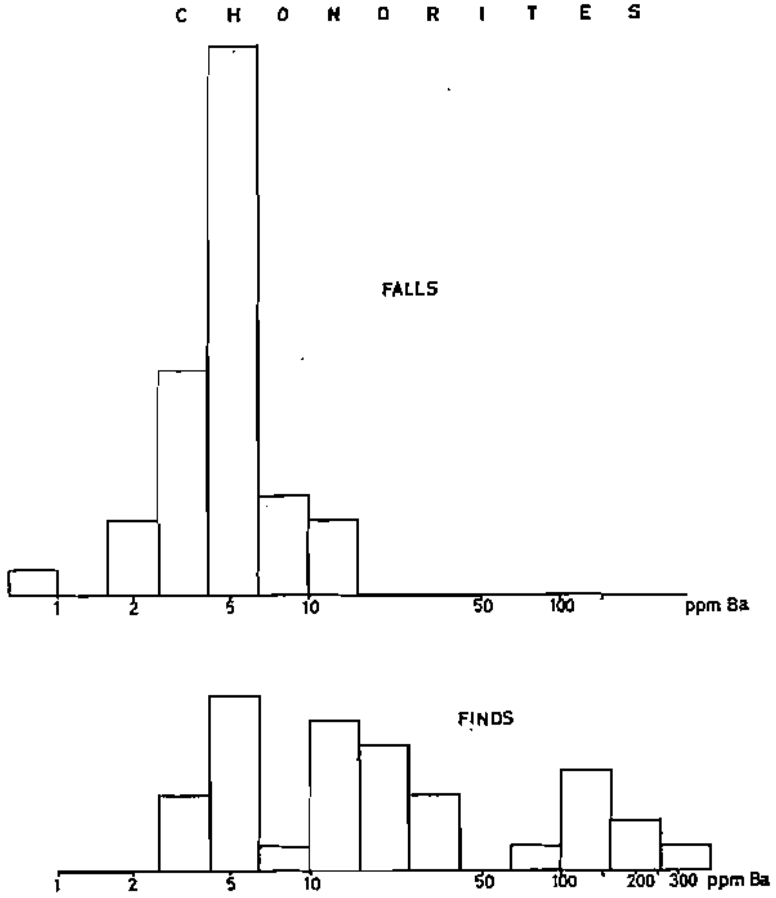

Fig. 56-C-1c. Distribution of Barium in ordinary chondrites, Class symbol CH

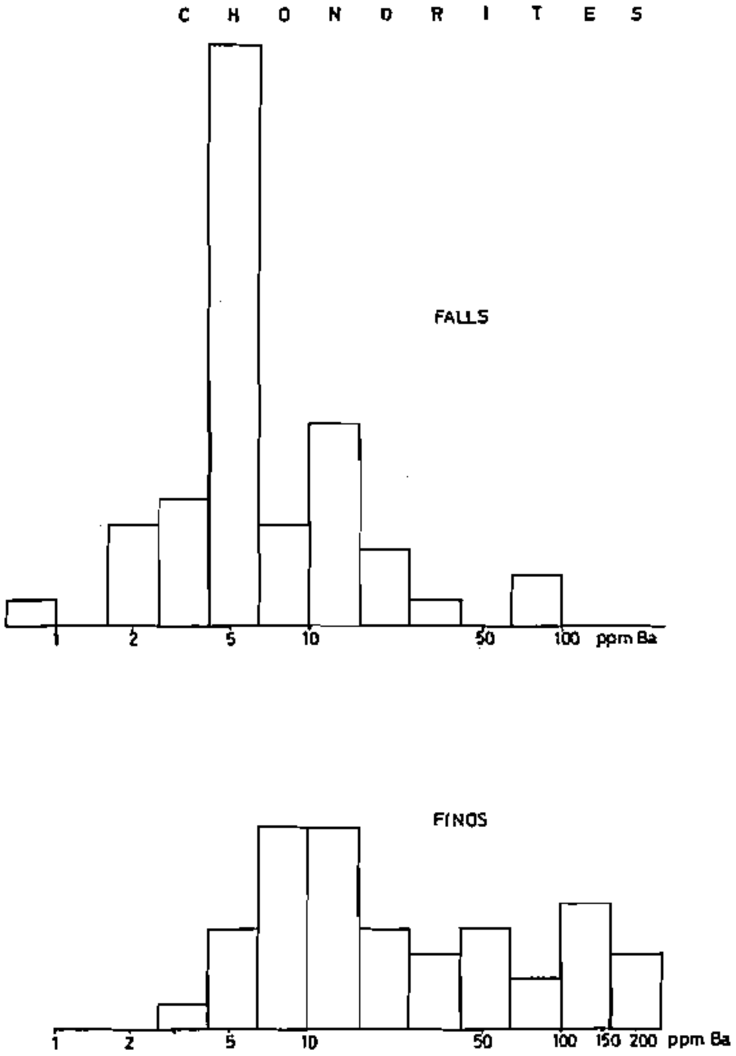

Fig. 56-C-1d. Distribution of Barium in ordinary chondrites, Class symbol CL

Calcium rich achondrites are also high in Ba, whereas Ca-poor achondrites show low Ba values, close to chondrites. In calculations of Ba averages in meteorites, the finds have to be omitted. The few data available for nonsilicate meteorite phases (all < 9 ppm) indicate that Ba is definitely a lithophilic element. Table 56-C-4 lists the mean concentrations of Ba in individual meteorite groups. Numbers of analyses used are given in brackets. Class CH and CL meteorites are by far the most frequent stony meteorites and by using their data, the Ba average for chondrites is calculated as 6.3 ppm.

Table 56-C-2. *Barium in stony meteorites*

Name of meteorite	Ba content ppm	Reference
Calcium poor achondrites		
Ae (falls):		
Cumberland Falls	14	10
Norton County	2	10
Ab (falls):		
Johnstown	2.5	10
	5	12
Shalka	4	10
Calcium rich achondrites		
Aor (falls):		
Bununu	18.5	11
Ab (falls):		
Juvinas	9—27	2
	26	1
	30.2	15
Moore County	17	1
	22	5
Pasamonte	26	1
	28.6—29.8	15
	38	5
	28.2	3
Sioux County	20	1
	25	5
	27.2	15
Stannern	62	1
	48	2
	53	15
Bereba	28.6	15
Jonzac	29—29.3	15
Angra dos Reis	21.5	15
Ap finds):		
Binda	2	1
Nuevo Laredo	40	1
	46	7
	44	13
	39.3	3
	39.3	15
Chondrites		
Ce_1 (falls):		
Abee	11.8	6
	1.8	13
	1.6	14
	2.41	3
	2.25	15
Indarch	6.4	6
	1.9	13
St. Marks	34.6	6
Ce_2 (falls):		
Hvittis	5.9	6
Khairpur	6.3	6
Pillistfer	5.5	6
CH (finds):		
Acme	120	10
Alamagordo	26	10
Aurora	20	10
Cavour	4	10
Colby (Kansas)	170	10
Coldwater	10	10
Cook	20.3	6
Coolidge	32	10
Covert	115	10
Dimboola	12.8	6
Estacado	6	12
Farley	290	10
Gladstone	17	10
Hugoton	200	10
Kaldoonera Hill	16.8	6
Kansas City	4	10
Kissij	5	8
Marsland	3	10
Modoc	3.6	7
	5	10
	3.8	13
Morland	5	10
Morven	10.1	6
Nardoo	12.9	6
Orlovka	18	10
Petropavlovka	4	10
Plainview	10	10
Ransom	28	10
	7	12
Seibert	125	10
Texline	13	10
Tulia	120	10
Wilmot	82	10
CH (falls)		
Alexandrowsky	10	10
Allegan	4.6	6
	4	10
Aviles	<1	2
Barbotan	1—3	2
Beardsley	5	10
	3	13
Beaver Creek	5	12
Cangas de Onis	5	12
Erxleben	1—3	2

Table 56-C-2. (Continued)

Name of meteorite	Ba content ppm	Reference
Forest City	3.37	3
	3.7	7
	4	10
	9	12
	3.3	13
	3.30—3.37	15
Forest Vale	4.3	6
Hessle	8	12
Ichkala	4	10
Kernouve	6	12
Kesen	4	10
Lumpkin	6	12
Monroe	5	12
Mount Browne	7.9	6
	4	10
Nanjemoy	13	10
Ochansk (1)	5	10
Ochansk (2)	2	10
Olmedilla de Alarcon	5	10
Pantar	4	4
	3	4
	5	10
	3.2	13
	2.9	13
Pultusk	3	10
	7	12
Richardton	3.2	7
	4	10
Uberaba	4	10
Weston	6	10
Yatoor	6	10
Zhovtnevyi	11.3	6
	6	10
CL (finds):		
Accalana	16.0	6
Adelie Land	11.3	6
Arriba	53	10
Asson	8	12
Barratta	6.6	6
	7	12
Beenham	34	10
Berdyansk	7	10
Bluff	3	10
Brisco	150	10
Cadell	5.8	6
Cocunda	10.0	6
Cook	40.6	6
Coolamon	46.5	6
De Nova	115	10
Goodland	10	10
Harrisonville	7	10
Hayes Center	32	12
	30	10
Herimitage Plains	52.4	6
Kingfisher	5	10
Kulnine	21.2	6
Ladder Creek	94	10
Lake Brown	8.4	6
La Lande	210	10
Long Island	100	12
	190	10
Loongana (Forest Lake)	13.1	6
McKinney	6	10
Melrose	155	10
Nardoo (2)	15.5	6
Ness County (1894)	20	10
Otis	7	10
Potter	155	10
Rawlinna	15	10
Roy	72	10
Rush Creek	5	10
Silverton (N.S. Wales)	10.3	6
Tryon	190	10
Vincent	15.8	6
Waconda	7	12
Yalgoo	18.2	6
CL (falls):		
Alfianello	3	10
Bjurböle	<1	2
	8	12
	5	10
	14.2	6
Bruderheim	3.37; 3.4	3
	4.3	14
	3.37	15
Chateau Renard	6	10
Chantonnay	1 to 3	2
Colby (Wisconsin)	4.5	10
Dhurmsala	6	10
Elenovka	5	10
	10.5	6
Farmington	9.1	6
Holbrook	2.7—9	2
	5.8	3
	12.2	6
	4	7
	26	10
	9	12
	3.6	13

Table 56-C-2. (Continued)

Name of meteorite	Ba content ppm	Reference	Name of meteorite	Ba content ppm	Reference
Homestead	11.0	12	Tané	5	10
	5.1	6	Tenham	15.8	6
Khohar	13.8	6	Tennasilm	10	12
Knyahinya	1—3	2	*CLL (falls):*		
	5	10	Ensisheim (light)	6.9	13
Krasnoi-Ugol	5	10	(dark)	7.1	13
Kuleschovka	3.5	10	Mangwendi	12.3	6
Kunashak	4	10	Olivenza	6	10
(light)	4.8	9	Savtschenkoje	4	10
(dark)	5.2	9	*CLL (finds):*		
L'Aigle	2.7—9	2	Kelly	165	10
Leedey	3.76; 3.85	3	Lake Labyrinth	9.9	6
	3.64—3.76	15	Shaw	26	10
Marion	3	10	*CHL:*		
Maziba	4	10	Felix	4	10
Mocs	21.7	6	Karoonda	11.9	6
	5	10	Lancé	21.8	6
	6	12		8.2	13
Narellan	7.6	6	Mokoia	9.5	6
New Concord	4	10	Warrenton	10.5	6
Ni Kolskoje	2	10	Cr_1:		
Olivenza	16.4	6	Orgueil	9.8	6
Parnallee	3.5	10		<1	12
Pavlograd	6.5	10		2.4	13
Perpeti	8.6	6	Hessle	8	12
Pervomaisky	5	10	Mighei	2.5	12
Saint Michel	13.3	6	Murray County	4	10
	4	10			
Saratov	22	10			
Stavropol	2.5	10			

References (methods in brackets): 1. DUKE and SILVER, 1967 (?); 2. VON ENGELHARDT, 1936 (S); 3. EUGSTER *et al.*, 1969 (I); 4. FREDRIKSON and KEIL, 1963 (S); 5. GAST, 1965 (I); 6. GREENLAND and LOVERING, 1965 (S); 7. HAMAGUCHI *et al.*, 1957 (N/R); 8. HEY, 1966 (?); 9. LAVRUKHINA *et al.*, 1966 (N/R); 10. MOORE and BROWN, 1963 (S); 11. PHILPOTTS *et al.*, 1967 (I); 12. PINSON *et al.*, 1953 (S); 13. REED, 1963 (N/R); 14. SHIMA and HONDA, 1967 (N/R); 15. TERA *et al.*, 1970 (I).

Table 56-C-3. *Barium in stony irons and irons*

Name of meteorite	Ba content ppm	Reference	Name of meteorite	Ba content ppm	Reference
M (fall):			*Om* (find):		
Estherville	5	1	Ni poor ataxite		
M (find):			Toluca (troilite)	<0.1	13
Pallasite olivine	7	12	El Taco	2.37	3
Og (find):			Octahedrite, Weekeroo Station	8.70	3
Canon Diablo (troilite)	0.4	13			
	<0.006	13			
	<0.3	13			

References: see Table 56-C-2.

Table 56-C-4. *Average Ba concentrations of stony meteorites*

		Falls	Finds
Ae	Enstatite achondrites	8 (2)	
Ab	Bronzite achondrites	3.8 (3)	
Ap	Pigeonite-plagioclase achondrites (eucrites)	30.0 (11)	34.2 (5)
Ce_1	Enstatite chondrites	8.6 (7)	
Ce_2	Enstatite chondrites	5.9 (3)	
CH	High iron (H)-group chondrites	4.9 (42)	43 (33)
CL	Low iron (L)-group chondrites	7.2 (53)	47.1 (42)

All calculations of Ba averages in meteorites suffer from one or both of the following uncertainties: inhomogeneity of the samples and difficulties in analytical methods. The first point was demonstrated by Moore and Brown (1963), when they analyzed different parts of the Holbrook chondrite, which was a fall. They got a range of 8 to 110 ppm Ba for the different parts of the specimen.

III. Tektites

Ba concentrations in tektites are reported to be in the range of 300 to 7,700 ppm (Table 56-C-5, Fig. 56-C-2). Older data which, are generally lower, are reviewed by Gmelin (1960). All the more recent papers show Ba values to be much higher in tektites than in any meteoritic material. Whereas most investigators found Ba con-

Table 56-C-5. *Barium in tektites and other natural glasses*

Locality	Ba concentration		No. of anal.	Method	Reference
	range	mean			
		Tektites			
Africa					
Ivory Coast	648—665	657	2	I	Schnetzler *et al.* (1967)
Asia					
Indomalaysia	300—320	310	2	S	Pinson *et al.* (1953)
Philippines	420		1	S	Pinson *et al.* (1953)
Indochina	900—2,000	1,300	6	S	Vorob'ev (1959)
Australia					
Australia	340—420	375	6	S	Chao (1963)
	540—800	620	43	S	Taylor and Sachs (1964)
	540—800	630	24	S	Taylor (1962)
Europe					
Czechoslovakia	2,000—7,700	3,600	10	S	Vorob'ev (1960)
North America					
Texas	370—1,100	610	21	S	Chao (1963)
	380—1,100	580	10	S	Cuttitta *et al.* (1967)
Georgia	340—715	566	7	S	Cuttitta *et al.* (1967)
Martha's Vineyard	390		1	S	Cuttitta *et al.* (1967)

Table 56-C-5. (Continued)

Locality	Ba concentration		No. of anal.	Method	Reference
	range	mean			
	Natural glasses				
Tasmania					
Darwin Glass	290—360	340	8	S	Taylor and Solomon (1964)
Darwin Glass, dark	550		1	M	Chapman *et al.* (1967)
Darwin Glass, light	300		1	M	Chapman *et al.* (1967)
Australia					
Macedon, dark	400		1	M	Chapman *et al.* (1967)
Macedon, light	200		1	M	Chapman *et al.* (1967)
Henbury impact glass	600—700	650	2	S	Taylor and Kolbe (1964)
Africa					
Bosumtwi Crater	533—624	579	2	I	Schnetzler *et al.* (1967)

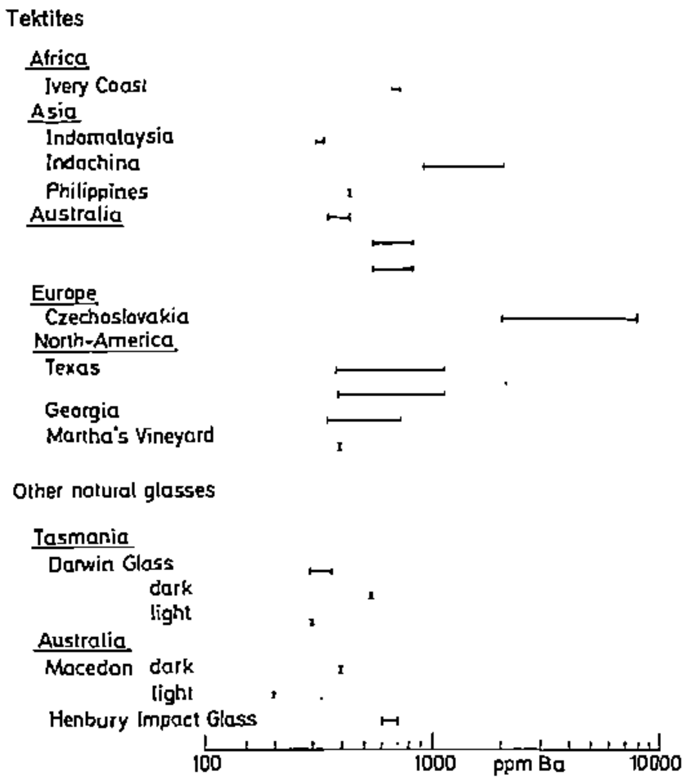

Fig. 56-C-2. Barium in tektites and other natural glasses

centrations in the range of 330 to 1,100 ppm, the values of Vorob'ev (1959, 1960) both for moldavites and indochinites are higher by a factor as great as ten, compared with tektite values from the same areas investigated by other scientists. Preuss (1935) gives a mean of 450 ppm Ba for 36 tektites, 14 of which were moldavites. Bouska and Povondra (1964) published semiquantitative spectrographic data for moldavites showing that six out of seven samples had 100 to 1,000 ppm Ba, and the other had less than 100 ppm Ba. Thus, it cannot be excluded that Vorob'ev's values are too high due to a systematic error, especially since no simple parent material can be imagined which would provide so much Ba. Taylor (1965, 1966) could relate australites by their Ba concentration and the content of other elements to Henbury impact glass and Henbury greywacke as parent materials. Similar investigations of Schnetzler *et al.* (1967) showed the consistency of Ba and RE concentrations in Ivory Coast tektites and Bosumtwi Crater impact glasses and strong similarities to Bosumtwi phyllites. Calculations by Taylor (1962) made it obvious that no meteorite splash could affect the Ba concentrations of the resulting impact glasses and tektites.

IV. Lunar Samples

Considerable effort has been expended on analytical investigations of lunar samples from Apollo 11 and 12 missions. From data of the individual investigators, averages were calculated for the different types of material according to the classification established by the *Lunar Sample Preliminary Examination Team* (1969, 1970), (Table 56-C-6).

The overall unweighted average for Apollo 11 material calculated from the means of the particular batches (33) is 240 ppm Ba, s = 76. The range of data for

Table 56-C-6. *Barium in lunar rocks*

Sample type	Barium content (ppm)		No. of analyses
	arith. mean	stand. dev.	
Apollo 11 (Mare Tranquillitatis):			
Type A: fine grained vesicular rocks	251	130	37
Type B: medium grained vuggy igneous rocks	176	72	23
Type C: breccia	230	66	37
Type D: "lunar soil" (fines)	169	40	16
Apollo 12 (Ocean of Storms)			
Basaltic rocks	72	50	13
Breccia	420	210	3
Fines	586	189	7
Sample 12013	3,088	2,256	24

References for Apollo 11 samples (methods in brackets): Annel and Helz (1970) (S); Brown *et al.* (1970) (X); Compston *et al.* (1970) (X); Gast *et al.* (1970) (I); Goles *et al.* (1970) (N/R); Haskin *et al.* (1970) (N/R); Maxwell *et al.* (1970) (S); Morrison *et al.* (1970) (N/R, M); Murthy *et al.* (1970) (I); Philpotts and Schnetzler (1970) (I); Smales *et al.* (1970) (I); Taylor *et al.* (1970) (S); Tera *et al.* (1970) (I); Wakita *et al.* (1970) (N/R); Wänke *et al.* (1970) (N/R).

Reference for Apollo 12 samples: Drake *et al.* (1970) (M); Hubbard *et al.* (1970) (I); Hubbard *et al.* (1971) (I); Lspet (1970) (S); Maxwell and Wiik (1971) (S); Schnetzler *et al.* (1970) (I); Wakita and Schmitt (1970) (N/R).

total rock analyses covers 10 to 370 ppm Ba, but values of upto 55,900 ppm and 24,400 ppm have been found (M) in interstitial K rich (9.4 and 10.9% K_2O) phases from a 4 mm fragment from lunar soil (10085-LR-1) (Albee and Chodos, 1970). These K rich phases consist predominantly of glass and extremely fine-grained crystalline material. Their chemical composition approaches but does not reach K feldspar composition. The K rich phase, which is present in about 6 vol.-% in sample 10085-LR-1, may also be responsible for Ba, Rb, and K concentrations in other samples, where a close relationship between these elements was observed. For several samples, a grouping to separate high K, Rb, Ba material from low K, Rb, Ba material has been tried. A few samples do not fit this separation. Still, the K/Ba ratios are rather constant in general. Inhomogeneities of Ba content in different chips of one sample have been reported, especially by Wakita *et al.*, N/R, (1970). Different chips of their batch 10019 differ by as much as 210 ppm in their Ba content (130 and 340 ppm). Analyses (N/R) of size fractions of lunar soil showed a Ba enrichment in the finer fraction (Wakita *et al.*, 1970).

Enrichment of Ba in moon rocks from Mare Tranquillitatis is 26 to 110 times (Gast *et al.*, 1970) compared to chondritic abundances. Within a single rock, concentration factors are similar for the "incompatable elements" Ba, U, Th, Zr, and REE except Eu.

Several individual minerals have been analyzed for Ba. The results are given in Table 56-C-7.

Apollo 12 samples from the Ocean of Storms show lower Ba content in the basaltic rocks (average 72 ppm), but higher values for breccia (average 420 ppm) and for "fines" (average 586 ppm). A most unusual rock is sample 12013 with 61% SiO_2, 2% K_2O and an average of 3088 ppm Ba. Microprobe investigations of individual points in alkali feldspars of this sample gave upto 8% BaO and 13.1% K_2O, i.e., compositions of celsian-orthoclase solid solution series (*Lunatic Asylum*, 1970). In rock 12013, Ba is enriched upto more than 2,000 times compared to chondrites (Hubbard *et al.*, 1970).

Table 56-C-7. *Ba content of individual minerals from Apollo 11 and 12 samples*

Mineral	Lunar sample	Ba concentration ppm	Method	Reference
Apollo 11:				
Plagioclase	10085	<1; <1; 15; 1,500	M	Andersen *et al.* (1970)
Plagioclase	10044—24	271	I	Philpotts *et al.* (1970)
Plagioclase	10062—29	70.1	I	Philpotts *et al.* (1970)
Clinopyroxene	10085	<1; 45	M	Andersen *et al.* (1970)
Pyroxene	10044—24	93.7	I	Philpotts *et al.* (1970)
Pyroxene	10062—29	30.9	I	Philpotts *et al.* (1970)
Ilmenite		81.2	I	Murthy *et al.* (1970)
Apollo 12:				
Plagioclase	12013	910	M	Drake *et al.* (1970)
Alk. feldspar	12013	10650	M	Drake *et al.* (1970)
Alk. feldspar	12013—10 (40)	895; 910; 8,680; 20,400	M	Lunatic Asylum (1970)

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56-D. Abundance in Rock-Forming Minerals (I) and Barium Minerals (II)

I. Rock-Forming Minerals

In igneous rocks of the earth's crust Ba usually does not form minerals of its own, but is distributed among a number of silicate structures, mainly feldspars and micas. The most important substitution is for potassium due to the nearly identical ion sizes, even with the somewhat more covalent character of the Ba—O bond. Substitution for Ca is observed in plagioclases, pyroxenes and amphiboles. Apatite and calcite are the most important rock forming non-silicates containing Ba.

a) Feldspars

K feldspars are the most important Ba carriers. Investigations by Roy (1965, 1967) and Gay and Roy (1968) with synthetic members have shown that a continuous series of solid solutions exist at high temperatures between K feldspars and celsian. In the subsolidus region, two gaps of miscibility seem to exist, one close to the microcline composition and the other between hyalophane and celsian (Fig. 56-D-1).

The system BaO—Al_2O_3—SiO_2 was recently investigated by Lin and Foster (1968, 1969).

In nature, K feldspars with BaO $>2\%$ are rare. They are mostly restricted to alpine type fissures (adularia) and deposits of manganese oxide.

Ba concentrations upto 9.5% in feldspars of the orthoclase-celsian series are reported from the alkalic rock complex, Magnet Cove (Erickson and Blade, 1963) and from phonolites in South West Germany (Weiskirchner, 1969). Ba distribution in K feldspars has been investigated by many authors. As a general pattern, it was found that in magmatic sequences the early crystallized K feldspars show the highest Ba concentrations, whereas microclines from pegmatites were low (S) in this element (Shimer, 1943; Bray, 1942). Metasomatic alteration of a granite body (Black Forest, Germany) was discussed as a cause of abundant K feldspar phenocrysts with a high and rather homogeneous Ba distribution by Emmermann (1968), (X).

Distribution of Ba abundances in K feldspars is shown for igneous rocks, pegmatites, and alpine fissures in Fig. 56-D-2 using the data of Table 56-D-1. The histograms clearly demonstrate that, in general, average pegmatitic K feldspars contain less Ba than those from granitic rocks.

Ba may enter the plagioclase structure depending on composition in the An-Ab series, temperature and pressure, of competing elements. Duchesne (1968) found a correlation between potassium and Ba concentrations. Many indications exist supporting the view that all the Ba in feldspars can be plotted in the four component system Ab, An, Or, Cn. Plots of Ba concentrations for different members

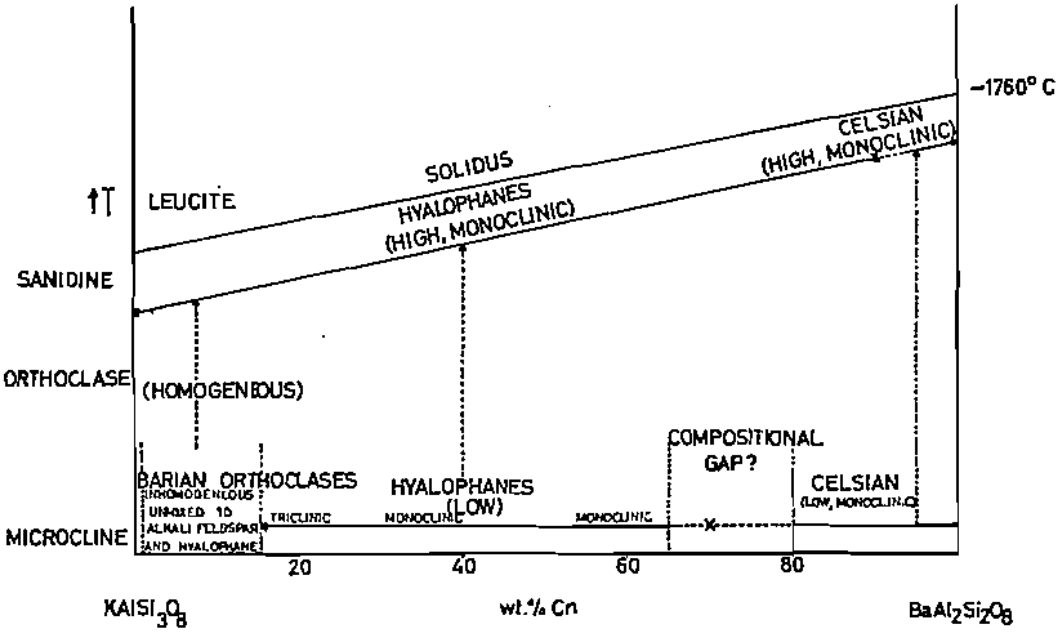

Fig. 56-D-1. Phases in the system $KAlSi_3O_8$—$BaAl_2Si_2O_8$ (GAY and ROY, 1968)

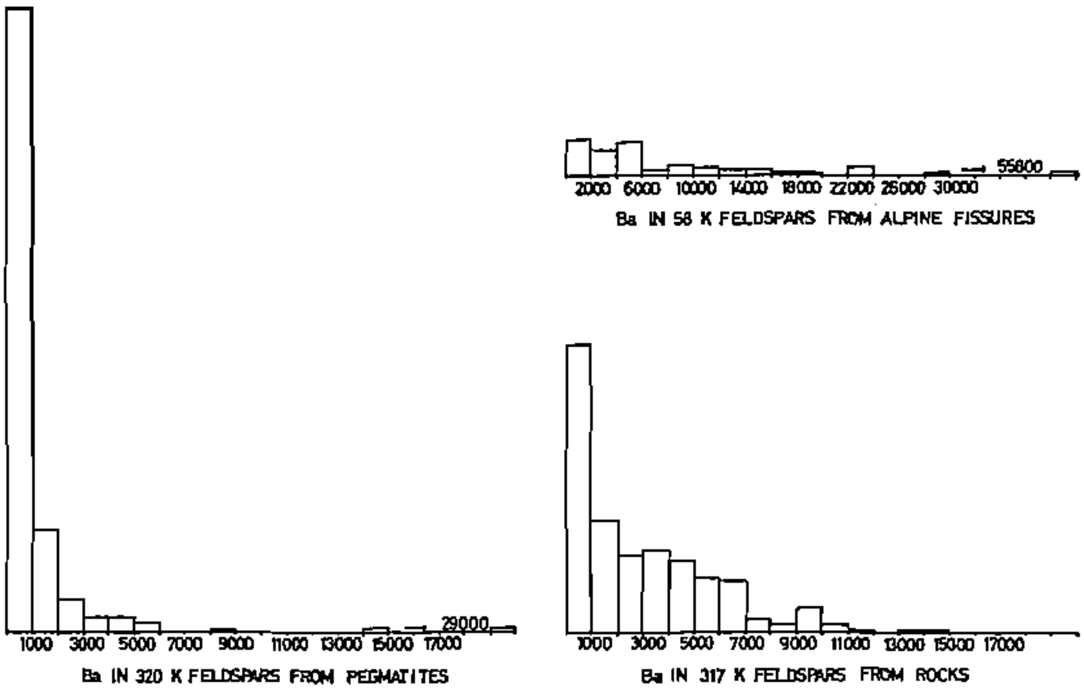

Fig. 56-D-2. Distribution of Ba concentrations in K feldspars (see Table 56-D-1 for references)

Table 56-D-1. *Barium concentrations in K feldspars*

Rock type	No. of analyses	Barium concentration range ppm	Barium concentration arith. mean	Method	Reference
Pegmatites	7	79— 1,130	270	S	Bray (1942)
	38	19— 450	100	X	Correia Neves (1964)
	6	3— 470	132	S	von Engelhardt (1936)
	5	200— 6,000	1,600	S	Erickson and Blade (1963)
	44	50— 3,400	710	S	Heier and Taylor (1959)
	17	20— 10,000	911	S	Higazy (1953)
	15	100— 1,700		S	Higazy (1949)
	5	435— 5,620	2,408	S	Hitchon (1960)
	9	190— 4,750	1,290	X	Markart and Preisinger (1964)
	11	150— 600	355	S	Oftedal (1961)
	40	150— 1,000	436	S	Oftedal (1962)
	44	< 10— 9,000	1,660	S	Oftedal (1958)
	16	171— 10,525	4,581	S	Pirani and Simboli (1963)
	64	76— 397	251	S	Shcherba *et al.* (1964)
	11	27— 3,550	495	S	Taylor *et al.* (1960)
	4	236—>6,000		S	Townend (1966)
		< 10— 10,525	*863*		*average for 320 samples*
Alpine fissures	13	220— 55,800	7,730	N	Rybach and Nissen (1967)
	3	2,400— 3,270	2,690	X	Markart and Preisinger (1964)
	15	2,600— 29,000	14,050	S	Weibel (1957)
	33	630— 15,300	5,000	S	Weibel and Meyer (1957)
	1	1,970	1,970	S	Hewlett (1959)
		220— 55,800	*7,481*		*average for 65 samples*
Igneous rocks					
Granite	11	162— 2,340	1,150	S	Bray (1942)
Granodiorite	4	322— 1,440	810	S	Bray (1942)
Quartzmonzonite	3	1,080— 1,260	1,170	S	Bray (1942)
Trachyte	2	5,100— 8,600	6,850	S	Carmichael (1965)
Granite	10	108— 361	201	S	Emiliani and Vespignani (1964)
Granite[a]	150	800— 5,400	4,700	X	Emmermann (1968)
Granite-larvikite	5	90— 14,300	3,920	S	von Engelhardt (1936)
Alkalic rock	4	900— 4,000	2,475	S	Erickson and Blade (1963)
Monzonite, granite	25	130— 12,000		S	Heier (1960)
Granite, gneiss	41	1,000— 9,500	3,840	S	Heier and Taylor (1959)
Granite, granodiorite, gneiss	12	90— 5,480	2,765	S	Herz and Dutra (1966)
Trachyte	10	360— 13,600	3,370	S	Hewlett (1959)
Granite	3	420— 2,700	1,550	S	Hewlett (1959)
Charnockite	4	2,500— 5,000		S	Howie (1955)
Monzonitic accumulate[b]	16	1,070— 12,100	5,000	X	Jasmund and Seck (1964)
Granite, gneiss	19	364— 4,620	2,220	X	Markart and Preisinger (1964)

Table 56-D-1. (Continued)

Rock type	No. of analyses	Barium concentration		Method	Reference
		range ppm	arith. mean		
Alkalic rock	4	630— 5,900	314	X	Perchuck and Ryabchikov (1968)
Granite	70	26— 9,480	2,124	X	Rhodes (1969)
Granite	9	4,350— 4,770	4,560	X	Richyer (1966)
Quartz, monzonitic	29	3— 3,000	990	S	Rogers (1958)
Granite	4	835— 1,020	950	S	Scharbert (1966)
Granite-tonalite	5	2,000— 3,000	2,500	S	Sen *et al.* (1959)
Granite	91	45— 392	176	S	Shcherba *et al.* (1964)
Granodiorite	14		836	S	Shcherba *et al.* (1964)
Adamellite	3		460	S	Shcherba *et al.* (1964)
Syenite	4		162	S	Shcherba *et al.* (1964)
Monzonite	2		155	S	Shcherba *et al.* (1964)
Syenodiorite	6		595	S	Shcherba *et al.* (1964)
Different rocks	32	< 200— 18,000	3,559	M	Smith and Ribbe (1966)
Different rocks[a]	23	< 200— 6,200	1,183	M	Smith and Ribbe (1966)
Granite	12	277—> 6,000		S	Townend (1966)
Granite	7	766— 1,526	1,240	X	White (1966)
		3— 18,000	*2,626*		*average for 598 samples*

[a] Sanidine.

of the plagioclase solid solution series show that the pure components contain less Ba than the intermediate plagioclases (Table 56-D-2, Fig. 56-D-3). This may be due to the fact that the pure end members are mostly very late or secondary crystals which formed from a Ba-poor liquid. Distribution of Ba between coexisting K feldspars and plagioclases is discussed as a potential geothermometer by Heier (1960, 1961). Barth (1961) showed that a straight line relation exists between log ratios of Ba in coexisting feldspars and log inverse absolute temperatures. He deduced that below 250° C, plagioclase is the preferred host mineral for Ba. Iiyama (1968) studied Ba distribution between potassium feldspars and plagioclases experimentally by hydrothermal runs at 600° C and 1,000 bars. His results contradict the observations in natural rocks as he finds higher Ba incorporation in the plagioclases than in the coexisting K feldspars. Rudert (1970) experimentally found an incorporation of Ba in albite at 930° C/1 kb, upto 30 weight % of celsian molecules; Bruno and Gazzoni (1970) substituted large amounts of Ca in the modifications of $BaAl_2Si_2O_8$. In the hexagonal modification synthesized by solid state reaction at 1,200° C, Ca replaces Ba upto 37% (atomic fraction); in the hexagonal modification obtained by crystallization of a melt, the replacement is limited to 25%; the same value was found for the monoclinic modification by heating the mentioned modifications to 1,450° C.

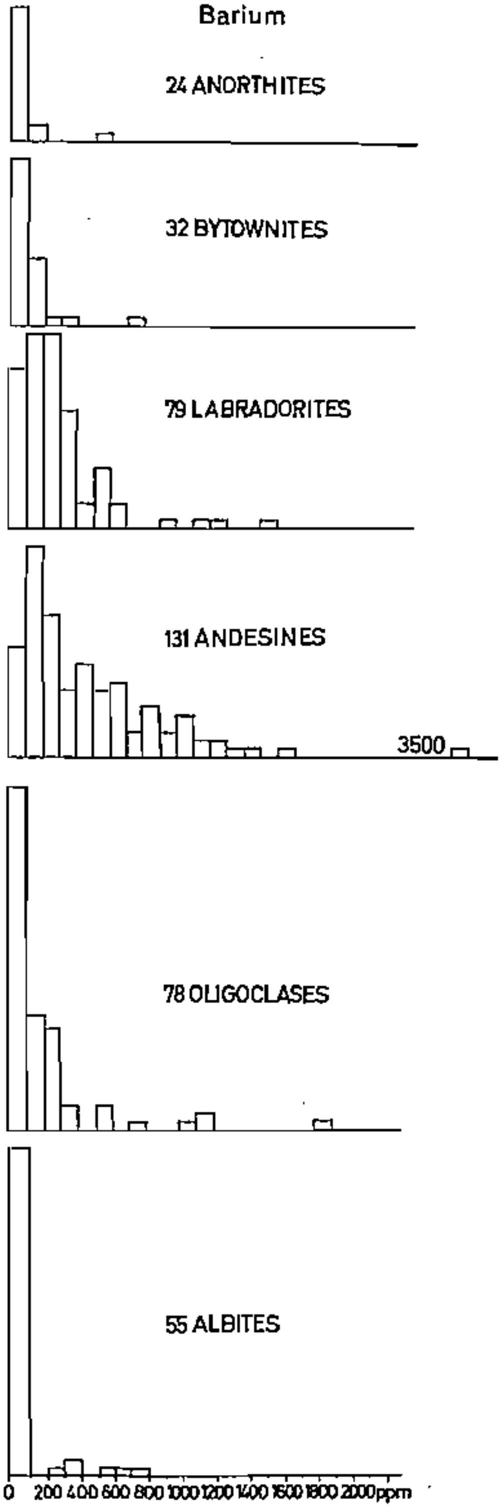

Fig. 56-D-3. Distribution of Ba concentrations in plagioclases (see Table 56-D-2 for references)

Table 56-D-2. *Barium concentrations in plagioclases from igneous and metamorphic rocks and rocks of hydrothermal origin*

Rock type	No. of analyses	Barium concentration range ppm		Barium concentration arith. mean	Method	Reference
Anorthites from:						
Basalt	1	60		60	S	Byers (1961)
Pumice	1	10		10	S	Coats (1952)
Anorthosite, gabbro and others	13	< 100—	500	< 217	M	Corlett and Ribbe (1967)
Metam. rock (amphibolite facies)	3	<45		<45	S	Sen (1960)
Metam. rock (granulite facies)	2	<45—	80	<60	S	Sen (1960)
Dacite-andesite	3	<45—	80	<63	S	Sen (1960)
Norite	1	10		10	S	Sen *et al.* (1959)
Bytownites from:						
Anorthosite, norite and others	12	<100—	100	<100	M	Corlett and Ribbe (1967)
Gabbro-anorthosite	9	40—	320	130	S	Emmons (1952)
Basalt	2	22—	270	146	S	Muir *et al.* (1964)
Metam. rock (amphibolite facies)	7	<45—	54	<46	S	Sen (1960)
Gabbro	2	80+	85	82	S	Sen *et al.* (1959)
Labradorites from:						
Anorthosite, gabbro and others	38	<100—	300	<195	M	Corlett and Ribbe (1967)
Basalt	9	200—	800	400	S	Cornwall and Rose (1957)
Gabbro-anorthosite	9	130—	580	347	S	Emmons (1952)
Anorthosite	2	85+	160	122	S	Papezik (1965)
Metam. rock (amphibolite facies)	3	115—	150	160	S	Sen (1960)
Metam. rock (granulite facies)	4	270—	480	295	S	Sen (1960)
Norite	3	45—	130	75	S	Sen *et al.* (1959)
Gabbro	2	50—	80	65	S	Wagner and Mitchell (1951)
Teschenite-basalt, gabbro	9	80—	1,500	451	S	Wilkinson (1959)
Andesines from:						
Anorthosite	9	630—	3,500	1,250	M	Anderson (1966)
Granite, granodiorite	6	370—	1,000	310	S	Bray (1942)
Gneiss, anorthosite and others	19	<100—	600	<177	M	Corlett and Ribbe (1967)
Granodiorite-anorthosite	5	90—	330	224	S	Emmons (1952)
Monzonitic accumulates	12	440—	1,020	735	X	Jasmund and Seck (1964)
Gneiss	11	900—	18,000	6,100	S	Oftedal (1958)
Pegmatite	12	10—	1,430	300	S	Oftedal (1958)
Anorthosite	10	150—	1,075	384	S	Papezik (1965)

Table 56-D-2. (Continued)

Rock type	No. of analyses	Barium concentration		Method	Reference
		range ppm	arith. mean		
Metam. rock (amphibolite facies)	15	<45— 990	<224	S	Sen (1960)
Metam. rock (granulite facies)	12	45— 700	380	S	Sen (1960)
Dacite-andesite	4	450— 870	560	S	Sen (1960)
Granite	2	250+ 320	285	S	Sen (1960)
Tonalite, granodiorite	6	80— 255	174	S	Sen *et al.* (1959)
Gabbro	6	200— 600	390	S	Wager and Mitchell (1951)
Teschenite, gabbro	2	350+ 600	475	S	Wilkinson (1959)
Oligoclases from:					
Anorthosite	1	3,480	3,480	M	Anderson (1966)
Pegmatite, granite and others	43	<100— 1,100	<134	M	Corlett and Ribbe (1967)
Basalt	2	700+ 1,000	850	S	Cornwall and Rose (1957)
Granite	4	70— 380	132	S	Emmons (1952)
Pegmatite	1	365	365	S	Hitchon (1960)
Granite	2	150— 268	209	S	Pirani and Simboli (1963)
Granite	4	180— 250	210	S	Scharbert (1966)
Metam. rock (amphibolite facies)	5	45— 540	205	S	Sen (1960)
Metam. rock (granulite facies)	7	<90— 1,170	<425	S	Sen (1960)
Rhyolite-rhyodacite	2	45— 1,800	922	S	Sen (1960)
Granite	5	63— 380	155	S	Sen (1960)
Granite, granodiorite	2	120+ 235	175	S	Sen *et al.* (1959)
Albites from:					
Pegmatite, alpine fissure	36	<100— 650	<145	M	Corlett and Ribbe (1967)
Basalt	1	700	700	S	Cornwall and Rose (1957)
Pegmatite	6	54— 80	69	X	Correia Neves (1964)
Pegmatite	1	1	1	S	Emmons (1952)
Pegmatite	1	2	2	S	von Engelhardt (1936)
Pegmatite	1	5	5	S	Higazy (1953)
Metam. rock (greenschist facies)	1	<45	<45	S	Sen (1960)
Different rocks	2	<200	<200	M	Smith and Ribbe (1966)
Pegmatite	5	12— 49	~24	S	Taylor *et al.* (1960)
Granophyre	1	30	30	S	Wager and Mitchell (1951)
Anorthoclases from:					
Basalt, trachyte	2	1,000+ 1,100	1,050	S	Wilkinson (1962)
Phonolite	1	2,160	2,160	S	Hewlett (1959)

b) Micas and Other Important Rock Forming Minerals

Micas are the next important Ba carriers in rocks. Ranges of Ba concentrations in these and other minerals are given in Table 56-D-3 and in Fig. 56-D-4. Ba is a concentrated in biotites as in muscovites. Only lepidolites have much lower Ba values. Generally micas from pegmatites show lower Ba values than those from the adjacent country rocks (TAKUBO and TATEKAWA, 1954), but each pegmatite may have its own "Ba level". Extensive material on Ba contents, mainly from pegmatite muscovites, was published by HEINRICH *et al.* (1956). These authors found Ba concentrations from 1 to 9,900 ppm in 162 samples, predominantly pegmatite muscovites. They calculated an average of 1,020 ppm Ba.

PETROV *et al.* (1965) found that the relative concentrations of Ba in biotites increase with metamorphic grade. In rocks free of K feldspars, biotite is often the main Ba carrier, sometimes together with pyroxenes and amphiboles. In skarns

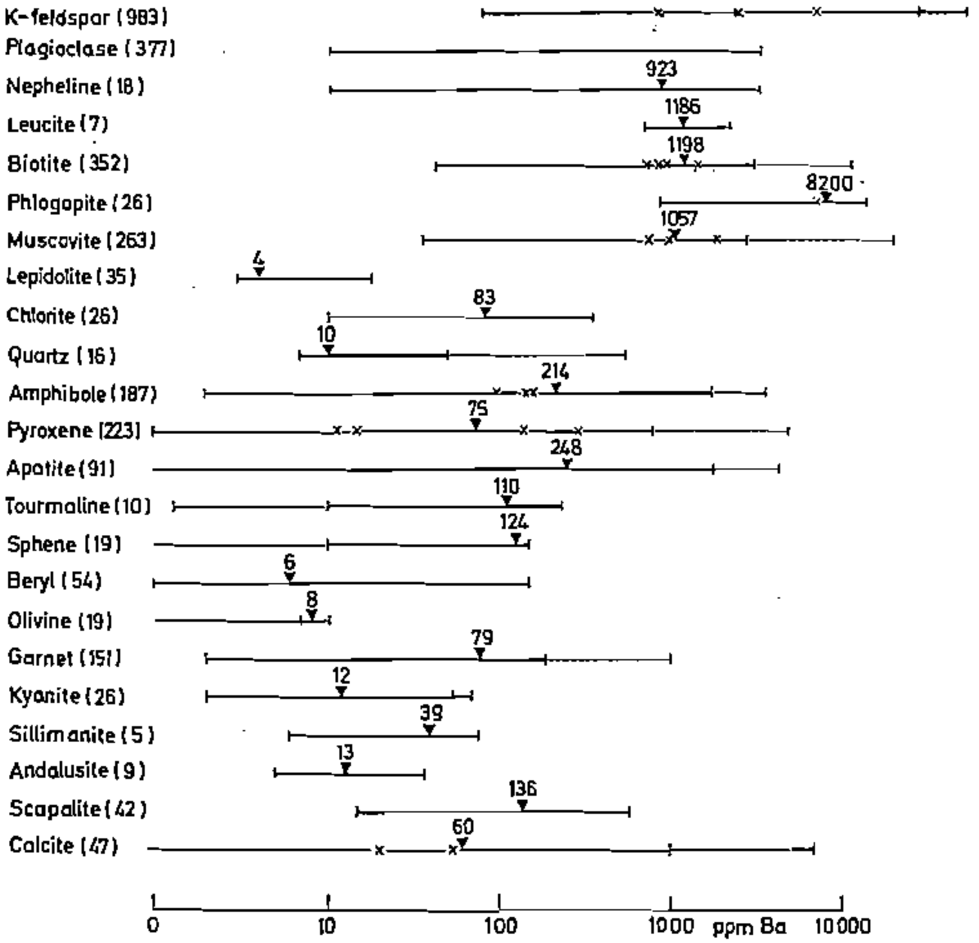

Fig. 56-D-4. Ba concentrations in rock forming minerals (see Table 56-D-4 for references). ▼ Indicates total averages. × Indicates group averages

Table 56-D-3. *Barium concentrations in rock forming minerals of igneous and metamorphic rocks*

Rock type	No. of analyses	Barium concentration range ppm	arith. mean	Method	Reference
Nepbeline					
Alkalic rock	3	<45— 3,320	1,270	S	von Eckermann (1952)
Alkalic rock	5	100— 3,000	1,200	S	Erickson and Blade (1963)
Pegmatite	6	<10— 20	20	S	Ofteoal (1962)
Alkalic rock	4	<100— 3,400	1,670	X	Perchuck and Ryabchikov (1968)
		<10— 3,400	*923*		*average for 18 samples*
Lencite					
Leucite-basanite	2	1,160— 1,250	1,200	S	von Engelhardt (1936)
Leucitopbyre-leucite basanite	5	710— 2,250	1,180	S	Henderson (1965)
		710— 2,250	*1,186*		*average for 7 samples*
Biotite					
Granite, granodiorite	12	67— 720	294	S	Bray (1942)
Pegmatite	3	103— 470	241	S	Bray (1942)
Schist	18	600— 1,100	790	S	Butler (1967)
Metapelite	5	500— 2,000	1,500	S	Caro (1964)
Rhyolite	8	1,430— 6,730	5,200	M	Carmichael (1967a)
Granitic rock	34	240— 5,000	1,405	S	Dooge *et al.* (1969)
Alkalic rock (carbonatite)	8	1,700— 6,360	4,065	S	von Eckermann (1952)
Granite	2	84+ 100	90	S	Emiliani and Vespignani (1964)
Paragneiss	25	300— 2,200	930	S	Engel and Engel (1960)
Alkalic rock	4	900—12,000	4,500	S	Erickson and Blaoe (1963)
Quartzdiorite-granite	13	400— 2,700	1,830	S	Haslam (1968)
Charnockite	2	900+ 2,300	1,600	S	Heier (1960)
Pegmatite	7	45— 2,320	717	S	Hitchon (1960)
Gneiss, schist, amphibolite	35	100— 1,200	750	S	Hunzicker (1966)
Gneiss, amphibolite	8	900— 3,180	~2,400	S	Kretz (1959)
Goeiss, schist	20	120— 2,450	810	S	Moxham (1965)
Pegmatite	3	200— 400	300	S	Ofteoal (1962)
Quartzmonzonite, granodiorite	24	450— 8,500	1,212	X	Rimsaite (1964)
Goeiss, schist	17	900— 2,700	808	X	Rimsaite (1964)
Metaarkose	7	472— 1,086	780	S	Schwarcz (1966)
Granite, norite	10	500— 2,500	1,822	S	Sen *et al.* (1959)
Pegmatite, wallrock	48	<150— 2,000	873	S	Stern (1966)
Metamorphic rock (staurolite zone)	22	42— 1,410	800	S	Turekian and Phinney (1962)
Migmatite, granite	8	240— 1,335	880	X	White (1966)
Basalt	1	2,500	2,500	S	Wilkinson (1962)
Cordierite-biotite, gneiss	8	60— 530	290	S	Wynne-Edwards and Hat (1962)
		42— 8,500	*1,198*		*average for 352 samples*

Table 56-D-3. (Continued)

Rock type	No. of analyses	Barium concentration range ppm	arith. mean	Method	Reference
Phlogopite					
Wyomingite, orendite	12	3,670—10,100	7,350	M	Carmichael (1967 b)
Wolgidite, wyomingite, fitzroyite	9	3,140—14,300	12,000	M	Carmichael (1967 b)
Alkalic rock	2	1,000+ 4,000	2,500	S	Erickson and Blade (1963)
Lamprophyre, basalt	3	2,700— 4,850	4,016	X	Rimsaite (1964)
		1,000—14,300	*8,202*		*average for 26 samples*
Muscovite					
Granite	7	108— 900	490	S	Bray (1942)
Pegmatite	5	23— 360	125	S	Bray (1942)
Schist	22	1,400— 2,900	1,930	S	Butler (1967)
Granite	2	1,000+ 1,100	1,050	S	Emiliani and Vespignani (1964)
Pegmatite	168	2— 9,800	1,020	S	Heinrich *et al.* (1953)
Pegmatite	1	36	36	S	Heinrich (1967)
Pegmatite	13		160	S	Hitchon (1960)
Gneiss, schist	14	110— 1,200	850	S	Hunzicker (1966)
Alpine fissure	2	230+ 300	265	S	Schwander *et al.* (1968)
Metamorphic rock	1	21,400	21,400	W	Snetsinger (1966)
Pegmatite	28	180— 1,650	797	S	Stern (1966)
		2—21,400	*1,057*		*average for 263 samples*
Lepidolite					
Pegmatite	26	2— 9	3	S	Heinrich *et al.* (1953)
Pegmatite	9	3— 18	7	S	Heinrich (1967)
		2— 18	*4*		*average for 35 samples*
Chlorite					
Basalt	11	20— 300	120	S	Cornwall and Rose (1957)
Granite	3	10— 50	25	S	Emiliani and Vespignani (1964)
Schist	11	17— 148 (2,100)	36	S	Gresens (1967)
Garnet, chlorite, schist	1	358	358	S	Mohr (1956)
		10— 2,100	*83*		*average for 26 samples*
Quartz					
Granite	4	280— 550	416	S	Bray (1942)
Pegmatite	11	30— 50	11	S	Hitchon (1960)
Basic intrusion	1	7	7	S	Wager and Mitchell (1951)
		7— 550	*112*		*average for 16 samples*
Amphibole					
Metamorphic rock (amphibolite)	3	<50— 200	100	S	Caro (1964)
Wolgidite, orendite	4	1,800— 5,400	3,700	M	Carmichael (1967b)

Table 56-D-3. (Continued)

Rock type	No. of analyses	Barium concentration range ppm	Barium concentration arith. mean	Method	Reference
Schist, glaucophane	9	2— 120	20	S	Coleman and Papike (1968)
Schist, riebeckite	4	<4— 140	74	S	Coleman and Papike (1968)
Schist, actinolite	2	12+ 410	211	S	Coleman and Papike (1968)
Granite	17	7— 50	30	S	Dodge *et al.* (1968)
Granodiorite, quartz-diorite	3	15— 95	60	S	Dodge *et al.* (1968)
Metamorphic rock (amphibolite)	24	24— 320	100	S	Engel and Engel (1962)
Diorite, porphyr	15	100— 300	150	S	Engel (1959)
Schist	13	44— 104	66	S	Gresens (1967)
Quartzdiorite	6	10— 36	20	S	Haslam (1968)
Granite	4	10— 36	20	S	Haslam (1968)
Rhyodacite	1	180	180	S	Haslam (1968)
Gneiss, schist	8	<10— 195 (1,200)	80	S	Hunzicker (1966)
Monzonitic accumulate	11	90— 1,780	755	X	Jasmund and Seck (1964)
Gneiss, amphibolite	16	<90— 300	160	S	Kretz (1959)
Amphibolite	9	<90— 360	230	S	Kretz (1960)
Gneiss, schist	20	10— 485	150	S	Moxham (1965)
Nepheline-syenite, pegmatite	2	10+ 20	15	S	Oftedal (1962)
Ophiolite	1	27	27	S	Plas and Hügi (1961)
Tonalite, granodiorite	12	10— 80	40	S	Sen *et al.* (1959)
Essexite	2	25— 150	90	S	Simpson (1954)
Basalt	1	100	100	S	Wilkinson (1962)
		2— 5,400	*214*		*average for 187 samples*
Pyroxene					
Basic layered rock	14	12— 22	18	S	Atkins (1969)
Basalt	1	60	60	S	Byers (1961)
Basalt etc.	8	30— 800	195	S	Cornwall and Rose (1957)
Alkalic rock	9	<45— 540	160	S	von Eckermann (1952)
Alkalic rock	32	<10— 5,000	300	S	Erickson and Blade (1963)
Peridotite	2	10— 18	14	S	Green (1964)
Quartzdiorite	4	5— 27	16	S	Haslam (1968)
Granite	1	10	10	S	Ishioka (1967)
Metamorphic rock (skarn)	10	<90— 360	<145	S	Kretz (1960)
Charnockite	20	<5— 22	≦11	S	Leelanandam (1967)
Basalt, trachyte	2	10+ 50	30	S	LeMaitre (1962)
Metamorphic rock (skarn)	38	<1— 44	12	S	Moxham (1960)
Basalt	8	5— 45	21	S	Muir *et al.* (1964)
Kimberlite	9	<10— 150	33	S	Nixon *et al.* (1963)

Table 56-D-3. (Continued)

Rock type	No. of analyses	Barium concentrations		Method	Reference
		range ppm	arith. mean		
Pegmatite	1	10	10	S	Oftedal (1962)
Olivine basalt	1	1.5	1.5	N/R	Onuma *et al.* (1968)
Metamorphic rock (skarn)	38	1— 65	15	S	Shaw *et al.* (1963)
Syenite, gabbro, essexite	5	<10— 30	<21	S	Simpson (1954)
Gabbro	9	<5— 60	16	S	Wager and Mitchell (1951)
Teschenite, basalt, gabbro	11	<5— 60	11	S	Wilkinson (1959)
		<1— 5,000	*75*		*average for 223 samples*

from the Greenville province, Kretz (1960) reports that the Ba content decreases in the following sequence: biotite > amphibole > pyroxene. The structure of chain silicates, where Ba occupies Ca positions, seems to accept more Ba at higher temperature of formation; Engel and Engel (1962) found an increasing Ba content (9, 18, 86, 106 ppm) in hornblendes from metamorphic rocks formed at 400, 500, 525, and 625° C.

Quartz has a rather low Ba content, and it is not certain whether contamination by other minerals was avoided in all analyses published.

From minerals of metamorphic origin, garnets exhibit the highest Ba values. Kyanites, sillimanites, and andalusites are much lower and always contain less than 100 ppm Ba.

Calcite from alkalic rocks in the form of carbonatites is somewhat enriched in Ba. Crystals from hydrothermal veins generally have very low Ba concentrations. The very rare Ca-Ba-carbonates, alstonite, barytocalcite, and benstonite are of no importance in rock formation and do not form solid solution series with the end members.

Depending on type and environment of formation, zeolites contain different amounts of Ba in their structures. Upto 300 ppm Ba were found in analcime and natrolite (Erickson and Blade, 1963; Wilkinson, 1959). In stilbite, thomsonite, chabasite, gmelinite, and gismandine, concentrations between 600 and 5,200 ppm Ba were reported (Hoss and Roy, 1960). Phillipsites, or constituents of the series phillipsite-harmotome, which occur in manganese nodules and in larger amounts in certain deep sea sediments, may be extremely enriched in Ba, upto 44,500 ppm (Shkabara, 1950; Hoss and Roy, 1960).

c) Barium Partition between Mineral and Host Rock and Between Coexisting Minerals

During the first stages of differentiation of basaltic magmas, Ba is enriched in the liquid phase. With progressing crystallization Ba is incorporated, especially in K feldspars and micas, which extract this element from the melt. Pegmatitic stages of differentiation series are consequently often impoverished in Ba.

Table 56-D-4. *Barium distribution between minerals and total rock*

Pair		No. of pairs	Barium concentration range		Distribution coefficient Ba_{min}/Ba_{rock}	Method	Reference
mineral	rock		mineral ppm	rock ppm			
Sanidine	Trachyte	7	140—6,900	120—1,800	1.17— 8.95	S	Berlin and Henderson (1969)
Plagioclase	Trachyte	5	560—3,500	770—1,100	0.72— 3.98	S	Berlin and Henderson (1969)
Anorthoclase	Phonolite	2	2,600—3,000	1,100—1,400	2.14— 2.37	S	Berlin and Henderson (1969)
Biotite	Dacite, rhyolite trachyte	8	1,400—6,700	400—1,100	1.6 — 15	M	Carmichael (1967a)
Garnet	Eclogite	11	150— 165	<10—1,140	0.13—>16.3	S	Hahn-Weinheimer and Lücke (1963)
Amphibole	Rhyodacite	1	180	580	0.31	S	Haslam (1968)
Biotite	Metaarkose	7	472—1,086	1,190—1,730	0.29— 0.65	S	Haslam (1968)
Pseudoleucite	Juvite, tinguaite	7	50—4,000	50—6,500	0.23— 1.00	X	Henderson (1965)
Leucite	Leucite-porphyre, leucite-basanite	5	710—2,250	1,950—2,250	0.36— 0.81	X	Henderson (1965)
Biotite	Amphibolite	9	575—1,150	270— 760	1.22— 4.60	S	Hunzicker (1966)
Biotite	Gneiss	19	290—1,150	250—1,050	0.40— 2.44	S	Hunzicker (1966)
Muscovite	Amphibolites	5	1,000—1,200	270— 760	1.33— 4.08	S	Hunzicker (1966)
Muscovite	Gneiss	9	390—1,100	310—1,050	0.85— 3.55	S	Hunzicker (1966)
Plagioclase	Granulite	12	110— 475	160—2,500	0.11— 3.37	S	Sen (1960)
Orthoclase	Granitic gneiss	5	3,330—5,380	706— 731	4.67— 7.38	X	White (1966)
Biotite	Granitic gneiss	2	847—1,110	706— 730	1.20— 1.52	X	White (1966)
Biotite	Biotite gneiss	8	60— 530	103— 380	0.41— 3.95	S	Wynne-Edwards *et al.* (1962)

Table 56-D-5. *Barium distribution between coexisting minerals*

Pairs		No. of pairs	Rock type	Range mineral I ppm Ba	Range mineral II ppm Ba	Range of distrib. coeffic.	Method	Reference
mineral I	mineral II							
Biotite	Muscovite	5	Gneiss, migmatite	1,250^{a}	630^{a}	1.98	X	1
		12	Schist, paragneiss	1,525^{a}	1,970^{a}	0.80	X	1
		18	Schist	600 — 1,100	1,400 — 2,900	0.31— 0.56	S	2
Biotite	Orthoclase	7	Migmatite, gneiss	240 — 1,335	1,176 — 6,718	0.20— 0.25	X	3
Biotite	Garnet	8	Paragneiss	350 — 2,200	35 — 1,100	2.00—15.0	S	4
		22	Metam. sequence (42)	580 — 1,410	11 — 38	21.0 —75.8	S	5
Biotite	Hornblende	5	Metamorphic rock	1,000 — 3,000	15 — 60	33 —68		6
		20	Gneiss, schist	120 — 2,450	10 — 485	2.50—60	S	7
Biotite (phlogopite)	Pyroxene	2	Phonolite, rhyodacite	2,480 + 4,670	21.3 + 55.0	116 +85	I	8
Biotite	Ilmenite	7	Metaarkose	472 — 1,086	7 — 132	0.01 — 0.28	S	9
Alk. feldsp.	Plagioclase	4	Trachyte	2,700 — 6,900	560 — 3,500	0.93 —10.8	S	10
Sanidine	Plagioclase	12	Monz. cumulates	900 —12,100	394 — 1,165	2.30 —15.9	X	11
Sanidine	Amphibole	11	Monz. cumulates	900 —12,100	90 — 1,770	1.50 —22.1	X	11
Orthoclase	Nepheline	3	Alkalic rock	990 — 2,300	100 — 3,400	0.38 —25.0	X	12
Plagiocl.	Amphibole	10	Monz. cumulates	395 — 1,170	415 — 1,780	0.51 — 1.69	X	11
Plagiocl.	Clinopyroxene	3	Oceanite, andesite	23 — 58.2	1.26— 10.2	4.75 —18.7	I	8
Pyroxene	Amphibole	5	Skarn	2.6— 26	12 —>500	<0.016— 2.00	S	13
Pyroxene	Scapolite	19	Skarn	1 — 31	14 — 210	0.013— 0.20	S	13
Clinopyrox.	Olivine	2 (6)	Ankoranite, alkali basalt	4.9— 175	1.9 — 5.1	2.59 —34.5	I	8

Reference: 1. RIMSAITE (1964); 2. BUTLER (1967); 3. WHITE (1966); 4. ENGEL and ENGEL (1960); 5. TUREKIAN and PHINNEY (1962); 6. HIETANEN (1971); 7. MOXHAM (1965); 8. PHILPOTTS and SCHNETZLER (1970a); 9. SCHWARCZ (1966); 10. BERLIN and HENDERSON (1969); 11. JASMUND and SECK (1964); 12. PERCHUCK and RYABCHIKOV (1968); 13. SHAW *et al.* (1963).

[a] average.

The degree of relative incorporation of an element into a specific mineral is given by the ratio:

$$D = \frac{\text{concentration of Ba in the phenocryst}}{\text{concentration of Ba in the melt}} .$$

This distribution coefficient can be calculated if equilibrium phenocrysts are compared with total ground mass, for instance, of volcanic rocks. If the amount of phenocrysts is low, the Ba content of the total rock can be used in the denominator of the above given equation. Distribution coefficients can also be calculated for metamorphic rocks, which constitute equilibrium mineral assemblages.

A number of these coefficients have been calculated from published data (Table 56-D-4). It must be mentioned that the distribution coefficients depend on several factors: pressure, temperature, the amount of Ba available, presence of competing elements, etc.

Berlin and Henderson (1969) determined Ba in sanidine and plagioclase crystals, and the embedding ground mass of trachytes and phonolites. They could reconstruct, by Ba and Sr determinations, the sequence of crystallization (sanidine or plagioclase first) and even detected in one case indications for secondary redistribution.

Philpotts and Schnetzler (1970a), analyzing (I) phenocrysts and a matrix of basic to intermediate volcanic rocks, calculated partition coefficients (Ba concentration in mineral/Ba concentration in matrix) for: plagioclases, $D = 0.0537$ to 0.589 (9 pairs); K feldspars, $D = 6.12$; clinopyroxenes, $D = 0.0129$ to 0.388 (10 pairs); orthopyroxenes, $D = 0.121$ and 0.141; micas (biotite-phlogopite), $D = 1.09$, 6.36 15.3; hornblendes, $D = 0.0996$, 0.417, 0.731; garnet, $D = 0.0172$; and olivines, $D = 0.00864$ and 0.0112. Only K feldspars and micas concentrate Ba relative to the matrix. They observed a strong coherence of Ba and K in almost all phenocrysts. The D-value of the K/Ba ratio is within the range of 0.5 to 2.0 in nearly all their examples. Since this K/Ba ratio is found to be extremely consistent in basic rock types, these authors recommend it as an "indexing criterion" for solar systems.

Ba distribution coefficients between coexisting minerals (Table 56-D-5) give some idea of the relative importance of minerals for the Ba content of a rock. It must be kept in mind that analyses of mineral phases isolated from a certain rock do not necessarily represent equilibrium conditions. Ba concentration in a definite mineral is affected by pressure, temperature, Ba availability, structure and position in the sequence of separation from the melt, and other parameters.

A useful index of fractionation is the ratio Ba/Rb. Ba has a tendency to be captured in early K minerals, whereas Rb is enriched in the residual melts due to its smaller charge and larger ion size. Taylor and Heier (1960) report a variation of the Ba/Rb ratio in feldspars from gneisses, granites and pegmatites from 54 to 0.04.

II. Barium Minerals

Because of their abundance, the most important Ba minerals and consequently the main Ba carriers in the earth's crust are: in igneous rocks, K feldspars, which contain a certain percentage of celsian molecules; and in sedimentary rocks and hydrothermal deposits, barite. Under special conditions, a large number of well defined Ba minerals can form. Sometimes they are reported from only one locality. In Table 56-D-6 the nonsilicates and silicates are listed. Criteria for the presentation in these lists have been: (1) reported by Strunz (1966), and/or (2) approved by the Commission on New Minerals of IMA.

Table 56-D-6. *Barium minerals*

Mineral	Formula
Oxides	
Billietite	$(BaO \cdot 6UO_3) \cdot 11H_2O$
Hollandite	$Ba_2\ Mn_8O_{16}$
Pandaite	$(Ba, Sr, Ca)(Nb, Ti, Ta)_2O_6 \cdot H_2O$
Priderite	$(K, Ba)_{1.3}(Ti, Fe)_8O_{16}$
Psilomelane	$(Ba, H_2O)Mn_5O_{10}$
Rijkeboerite	$Ba_{1-x}(Ta, Nb)_2O_6(H_2O)$
Todorokite	$(Mn, Mg, Ca, Ba, Na, K)_2Mn_5O_{12} \cdot 3H_2O$
Carbonates	
Alstonite (Ba-aragonite)	$BaCa[CO_3]_2$
Barytocalcite	$BaCa[CO_3]_2$
Benstonite	$(Ca, Mg, Mn)_7(Ba, Sr)_6[CO_3]_{13}$
Burbankite	$(Na, Ca, Sr, Ba, Ce)_6[CO_3]_5$
Carbocernaite	$(Ca, RE, Na, Sr, Ba)[CO_3]$
Ewaldite	$Ba(Ca, RE, Na, K, Sr, U, \square)[CO_3]_2$
Huanghoite	$BaCe[CO_3]_2F$.
Kordylite	$Ba(Ce, La, Nd)_2F_2/[CO_3]_3$
Mckelveyite	$Na_2Ba_4CaY_2[CO_3]_9 \cdot H_2O$
Norsethite	$BaMg[CO_3]_2$
Stenonite	$(Sr, Ba, Na)_2Al[CO_3]F$
Witherite	$BaCO_3$
Nitrate	
Nitrobarite	$Ba[NO_3]_2$
Sulfate[a]	
Barite	$BaSO_4$
Selenite	
Guilleminite	$Ba(UO_2)_3[SeO_3]_2(OH)_4 \cdot 3H_2O$
Phosphates, Arsenates, Vanadates	
Babefphite	$Be_6Ba_4[PO_4]_4O\ F_4 \cdot 0.35H_2O$
Bergenite[b]	$Ba(UO_2)_4[PO_4]_2(OH)_4 \cdot 8H_2O$
Dussertite	$BaFe^{3+}{}_3H[AsO_4]_2(OH)_6$
Ferrazite[c]	$(Pb, Ba)_3[PO_4]_2 \cdot 8H_2O$
Francevillite	$(Ba, Pb)(UO_2)_2[VO_4]_2 \cdot 8H_2O$
Gamagarite	$Ba_4(Fe, Mn)_2V_4O_{15}(OH)_2$
Gorceixite	$BaAl_3(OH)_5[PO_4]_2 \cdot H_2O$
Heinrichite	$Ba(UO_2)_2[AsO_4]_2 \cdot 10H_2O$
Metaankoleite	$(K, Ba)(UO_2)_2[PO_4]_2 \cdot 6H_2O$
Metaheinrichite	$Ba(UO_2)_2[AsO_4]_2 \cdot 8H_2O$
Metauranocircite I	$Ba(UO_2)_2[PO_4]_2 \cdot 8H_2O$
Metauranocircite II	$Ba(UO_2)_2[PO_4]_2 \cdot 6H_2O$
Strontiumapatite[b]	$(Sr, Ba)_6(Ca, RE, Mg, Na)_4[PO_4]_6(F, OH)_2$
Uranocircite I	$Ba(UO_2)_2[PO_4]_2 \cdot 12H_2O$
Uranocircite II	$Ba(UO_2)_2[PO_4]_2 \cdot 10H_2O$
Vesignietite	$BaCu_3[VO_4]_2(OH)_2$
Weilerite[d]	$BaAl_3H_{0-1}[AsO_4, SO_4]_2(OH)_{7-6}$

Table 56-D-6. (Continued)

Mineral	Formula
Nesosilicates	
Bariumuranophane	$BaH[UO_2/SiO_4]_3 \cdot 5H_2O$
Garrelsite	$(Ba, Ca)_4H_6Si_2B_6O_{20}$
Sorosilicates	
Bafertisite	$BaFe_2TiSi_2O_9$
Barylite	$BaBe_2Si_2O_7$
Hyalotektite	$(Pb, Ca, Ba)_4B[Si_6O_{17}](F, OH)$
Innelite	$Ba_2(Na, K, Mn, Ti)_2Ti(O, OH, F)_2[(S, Si)O_4/Si_2O_7]$
Labuotsovite	$(K, Ba, Na)(Ti, Nb)(Si, Al)_2(O, OH)_7 \cdot H_2O$
Nenandkevichite	$(Na, K, Ca, Ba)(Nb, Ti)[Si_2O_7] \cdot 2H_2O$
Shcherbakovite	$(K, Na, Ba)_3(Ti, Nb)_2[Si_2O_7]_2$
Yoshimuraite	$(Ba, Sr)_2(Mn, Fe, Mg)_2(Ti, Fe)(OH, Cl)_2[(S, P, Si)O_4/Si_2O_7]$
Ring silicates	
Armenite	$BaCa_2Al_6Si_8O_{28} \cdot 2H_2O$
Baotite	$Ba_4(Ti, Nb)_8Si_4O_{28}Cl$
Benitoite	$BaTiSi_3O_9$
Cappelenite	$(Ba, Ca, Ce, Na)_3(Y, Ce, La)_6[BO_3]_6[Si_3O_9]$
Muirite	$Ba_{10}Ca_2MnTiSi_{10}O_{30}(OH, Cl, F)_{10}$
Papstite	$Ba(Sn, Ti)Si_3O_9$
Taramellite	$Ba_2(Fe^{3+}, Ti, Fe^{2+})_2(OH)_2[Si_4O_{12}]$
Traskite	$Ba_9Fe_2Ti_2Si_{12}O_{36}(OH, Cl, F)_6 \cdot 6H_2O$
Verplanckite	$Ba_2(Mn, Fe, Ti)Si_2O_6(O, OH, Cl, F)_2 \cdot 3H_2O$
Chain silicates	
Batisite	$Na_2BaTi_2[Si_2O_7]_2$
Krauskopfite	$BaSi_2O_5 \cdot 3H_2O$
Walstromite	$BaCa_2Si_3O_9$
Sheet silicates	
Anandite	$(Ba, K)(Fe, Mg)_3(Si, Al, Fe)_4O_{10}(O, OH)_2$
Bariumphlogopite	$(K, Ba)Mg_3(F, OH)_2[AlSi_3O_{10}]$
Barium-vanadium-muscovite	$(K, Na, Ba)(Al, Ti, V, Mg)_2(OH)_2[AlSi_3O_{10}]$
Gillespite	$BaFe[Si_4O_{10}]$
Oellacherite	$(K, Ba)(Al, Mg)_2\ (OH, F)_2[AlSi_3O_{10}]$
Sanbornite	$Ba_2[Si_4O_{10}]$
Tectosilicates (without zeolites)	
Banalsite	$BaNa_2[Al_2Si_2O_8]$
Celsian	$Ba[Al_2Si_2O_8]$
Paracelsian	$Ba[Al_2Si_2O_8]$
Bariumalbite	solid solution Ab-Or-Ce
Bariumplagioclase	solid solution Ab-An-Ce
Calciocelsian	solid solution Ce-An
Hyalophane	solid solution Or-Ce
Bariumsanidine	solid solution
Cymrite	$BaAlSi_3O_8(OH)$
Wenkite	$(Ba,Ca)_9[SO_4]_2Al_9Si_{12}O_{42}(OH)_5$

Table 56-D-6. (Continued)

Mineral	Formula
Zeolites	
Barium heulandite	$(Ca,Ba)[Al_2Si_7O_{18}] \cdot 6H_2O$
Brewsterite	$(Sr, Ba, Ca)_2\ Al_4Si_{12}O_{32} \cdot 10H_2O$
Edingtonite	$Ba\ Al_2Si_3O_{10} \cdot 3H_2O$
Harmotome	$Ba_2\ Al_4Si_{12}O_{32} \cdot 12H_2O$
Wellsite	solid solution phillipsite-harmotome
Unclassified silicates	
Fresnoite	$Ba_2TiSi_2O_8$
Joaquinite	$NaBa(Ti, Fe)_3Si_4O_{15}$
Leukosphenite	$BaNa_4(TiO)_2[Si_2O_5]_5$
Macdonaldite	$BaCa_4Si_{15}O_{35} \cdot 11H_2O$
Tienshanite	$Na_2BaMnTiB_2Si_6O_{20}$

Calciobarite (Ca), Baritocelestite, Celestobarite (Sr), Baritoanglesite, Anglesobarite, Hokutolite, Weisbachite (Pb), Radiobarite (Ra). Reviews on composition, occurence, and crystallographic and physical properties are given by DANA (1951), HINTZE (1930, 1938, 1960). X-ray evidence for the existence of a barite-celestite isomorphous series has been obtained by SABINE and YOUNG (1954).

BOSTRÖM *et al.* (1968) studied subsolidus phase relations and lattice constants in the system $BaSO_4$-$SrSO_4$-$PbSO_4$.

[a] Barite forms more or less continuously, solid solutions with Ca, Sr, Ra, and Pb sulfates. In keeping with respective compositions, different names are used for the members of the series:

[b] No decisive vote of the IMA new mineral commission.

[c] Doubtful mineral species.

[d] Not yet approved by IMA new mineral commission.

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56-E. Abundance in Common Igneous Rock Types

A survey of Ba concentrations of rocks published by v. Engelhardt (1936) showed that Ba content in igneous rock series normally increases with increasing SiO_2 concentration. Recent data of Ba concentrations in common igneous rocks are summarized in Tables 56-E-1 and 2. The grouping follows the outlines of Wedepohl in volume 1 of this handbook. The listing contains the range of individual values, the arithmetic means and the standard deviation (s) of these means. Ba distribution in the main rock types is briefly discussed, as well as its bearing on genetic interpretations.

I. Ultramafic Rocks

The most important ultramafic rocks in the development of magmatic series are dunites and peridotites. From the available data, mostly spectrographic, an average of 8.8 ppm for dunite and of 25 ppm for peridotite was calculated. In their table of elemental distribution in the earth's crust, Turekian and Wedepohl (1961) preferred a neutron activation value of 0.4 ppm Ba for dunite rather than a spectrographic determination average of 6 ppm.

All data for these rocks suffer from potential contamination (see discrepancy between finds and falls of chondrites) and from analytical difficulties occurring close to the detection limit of Ba.

Pyroxenites contain a little more Ba (average 23 ppm); biotite pyroxenites have concentrations upto 3,200 ppm Ba (Higazy, 1954), as do kimberlites, where phlogopite is the main Ba carrier. Very high values are also reported for carbonatites (average 3,520 ppm) which sometimes even contain barite.

II. Gabbroic and Basaltic Rocks

Gabbroic rocks of intrusive occurence (average Ba content 246 ppm) closely resemble continental tholeiitic basalts (average Ba content 246 ppm).

Basalts can be divided into three groups according to their trace element concentration (Fig. 56-E-1). The averages for Ba are as follows:

Oceanic tholeiitic basalts	14.5 ppm Ba
Tholeiitic basalts of continents and oceanic islands	246 ppm Ba
Alkali basalts	613 ppm Ba.

All trace element data for oceanic tholeiitic basalts indicate a general uniformity for widely separated parts of the oceans. Muir *et al.* (1964), however, determined Ba from the rift zone of the Midatlantic Ridge, at 45° N, and found 55 to 220 ppm (S). The continental tholeiitic basalts contain more Si, K, Ba, Cs, Pb, and Rb than oceanic tholeiitic basalts (Gast, 1960).

Table 56-E-1. *Barium in intrusive rocks*

Rock type	No. of localities or No. of mean values used	No. of individual values	Range of individual values in ppm	Arith. mean of means grouped by locality in ppm	s[a]	References[b]
Alkali granite	3	19	22— 2,100	857		11, 12, 73
Granite	28	608	22— 3,000	732	453	6, 17, 21, 24, 26, 31, 32, 49, 50, 54, 55, 57, 62, 67, 72, 73, 75, 80, 83, 85, 87, 89, 93, 106, 121, 126
Granodiorite	7	53	400— 1,815	888		6, 73, 83, 87, 124, 131
Quartzdiorite	5	18	150— 1,250	811		87, 90, 131
Quartzmonzonite	3	18	233— 6,000	1,605		12, 87, 124
Alkali syenite	4	10	300— 2,070	1,067		21, 34, 75, 109
Syenite	9	30	230—18,000	2,753		24, 34, 44, 58, 63, 97, 100, 109, 111
Monzogabbro	1	4	7,500—14,000	10,360		100
Diorite	3	25	126— 1,150	714		75, 87, 90
Gabbro	10	148	5— 1,250	246	228	4, 21, 75, 87, 91, 100, 101, 109, 111, 127
Anorthosite	3	66	65— 475	171		75, 91
Norite	4	18	5— 310	78		75, 87, 99
Nepheline syenite	12	524	10— 6,300	1,427	1,206	27, 34, 35, 43, 44, 58, 59, 61, 75, 111, 125
Essexite	3	8	850— 2,800	1,598		64, 88, 111
Teschenite	1	3	650— 2,000	1,500		63
Ijolite, melteigite, jacupyrangite	5	66	88— 2,430	973		27, 35, 43, 44, 75
Dunite	9	18	0.3— 40	8.8		34, 39, 56, 75, 98, 100
Peridotite	6	9	1— 70	38		38, 39, 64, 75, 98
Pyroxenite	2	13	5.5— 67	23		75, 98
Kimberlite	4	35	20— 2,860	847		23, 29, 53, 68
Carbonatite	9	215	88—54,000	3,799		23, 27—29, 35, 41, 46, 64, 69, 105, 123

[a] s is the standard deviation of the mean values of the different authors, standard deviations are given only when 10 or more mean values were available.

[b] For list of references see Page 56-E-4.

Table 56-E-2. *Barium in volcanic rocks*

Rock type	No. of localities or No. of mean values used	No. of individual values	Range of individual values in ppm	Arith. mean of means grouped by locality in ppm	s[a]	References[b]
Alkali rhyolite	8	126	1— 700	118		25, 30, 36, 86, 102, 103, 109
Rhyolite	20	153	5— 3,650	1,127	632	8, 9, 18, 25, 26, 30, 74, 79, 88, 89, 92, 103, 108, 109, 112, 121
Rhyodacite	3	12	550— 1,800	1,210		18, 30, 89
Dacite	7	22	150— 1,250	629		87, 89, 118, 122
Quartz latite	1			550		112
Alkali trachyte	2	2	800+ 1,500	1,150		88, 128
Trachyte	10	30	20— 3,000	1,177	667	3, 36, 71, 88, 92, 107, 128
Latite minette	3	4	137— 2,500	1,379		18, 88, 112
Latite andesite	2	7	300— 2,250	841		88, 112
Andesite	23	185	80— 2,700	703	475	2, 3, 8, 39, 45, 51, 74, 79, 88, 89, 108, 110, 112, 115, 118, 120, 122, 128
Tholeiitic basalt	51	555	20— 1,160	246	197	3, 5, 8, 10, 13—16, 19, 20, 22, 37, 48, 51, 52, 60, 65, 74, 76, 77, 81, 87—89, 92, 94—96, 99, 113, 114, 117, 119, 127, 128
Alkali basalt	16	100	30— 1,350	613	223	1, 3, 33, 51, 66, 76, 78, 81, 88, 116, 117, 129, 130, 132
Oceanic tholeiite	41	41	3— 46	14.5	11.3	33, 42, 70, 82, 84
Phonolite	5	42	10— 2,000	999		27, 44, 71, 88, 104
Nepheline basanite Nepheline tephrite Leucite basanite Leucite tephrite	8	95	250— 9,360	1,976		7, 40, 64, 88, 104, 107, 130, 133
Nephelinite	2	5	600— 5,900	3,444		64, 130
Ankaratrite	1	2	1,800+ 4,000	2,900		64
Leucitite	1	9	1,800— 7,000	3,510		64
Melilitite	1	2	2,200+10,000	6,100		64
Alnöite	2	22	450— 6,930	1,890		27—29, 47

[a] s is the standard deviation of the mean values of the different authors, standard deviations are given only when 10 or more mean values were available.

[b] For list of references see Page 56-E-4.

References (methods in brackets): 1. Baker, 1969 (X); 2. Baker, 1968 (S); 3. Baker *et al.*, 1964 (S); 4. Baragar, 1960 (S); 5. Bartel *et al.*, 1963 (S); 6. Bräuer, 1965; 7. Brown and Carmichael, 1969 (X); 8. Byers, jr., 1961 (S); 9. Carmichael and McDonald, 1961 (S); 10. Clarke, 1970; 11. Clifford *et al.*, 1962 (S); 12. Clifford *et al.*, 1969 (S); 13. Coats, 1952 (S); 14. Coats, 1953 (S); 15. Coats, 1959 (S); 16. Coats *et al.*, 1961 (S); 17. Cocco, 1953 (S); 18. Cornwall, 1962 (S); 19. Cornwall and Rose jr., 1957 (S); 20. Cox and Hornung, 1966 (S, X); 21. Cox *et al.*, 1965 (S); 22. Cox *et al.*, 1967 (S); 23. Dawson, 1962 (S); 24. Dietrich and Heier, 1967; 25. Dixon *et al.*, 1968 (S); 26. Dunham, 1968 (S); 27. v. Eckermann, 1948 (S); 28. v. Eckermann, 1966 (S); 29. v. Eckermann, 1967 (S); 30. El-Hinnawi, 1969 (S); 31. Emiliani and Vespignani, 1964 (S); 32. Emmermann, 1968 (X); 33. Engel *et al.*, 1965 (S); 34. v. Engelhardt, 1936 (S); 35. Erickson and Blade, 1963 (S); 36. Ewart *et al.*, 1968 (S); 37. Fairbairn *et al.*, 1953 (S); 38. Fisher and Engel, 1969 (S); 39. Flanagan, 1969 (S, N/R, X); 40. Fornaseri *et al.*, 1963 (W); 41. Garson, 1967; 42. Gast, 1965; 43. Gerasimovskii, 1966 (S); 44. Gerasimovskii and Belyaev, 1963 (S); 45. Giusca and Ionescu, 1965; 46. Gold, 1963; 47. Gold, 1967; 48. Greenland and Lovering, 1966 (S); 49. Grohmann and Schroll, 1966 (S); 50. Grout, 1935 (W); 51. Gunn, 1965 (X); 52. Gunn, 1966 (X); 53. Hahn-Weinheimer, 1959 (S); 54. Hahn-Weinheimer and Ackermann, 1967 (X); 55. Hall, 1967 (X); 56. Hamaguchi *et al.*, 1957 (N/R); 57. Heier, 1960 (S); 58. Heier, 1964 (S); 59. Heier, 1965 (S); 60. Heier *et al.*, 1966 (S); 61. Henderson, 1965 (S); 62. Herz and Dutra, 1960 (S); 63. Higazy, 1952 (S); 64. Higazy, 1954 (S); 65. Hotz, 1953 (S); 66. Huckenholz, 1969 (X); 67. Hügi and Swaine, 1963 (S); 68. Janse, 1962; 69. Johnson, 1961 (S); 70. Kay *et al.*, 1970 (I); 71. King and Sutherland, 1967; 72. Kolbe, 1964; 73. Kolbe and Taylor, 1966 (S); 74. Kuno *et al.*, 1957 (S); 75. Liebenberg, 1960 (S); 76. Lipman, 1969 (S); 77. MacDonald and Eaton, 1964 (S); 78. Le Maitre, 1962 (S); 79. Markhinin *et al.*, 1964 (S); 80. Marmo and Siivola, 1966 (S); 81. Mathias, 1957 (S); 82. Melson *et al.*, 1968 (S); 83. Moenke, 1960 (S); 84. Muir *et al.*, 1964 (S); 85. Mukherjee, 1968 (S); 86. Noble and Haffty, 1969 (S); 87. Nockolds and Allen, 1953 (S); 88. Nockolds and Allen, 1954 (S); 89. Nockolds and Allen, 1956 (S); 90. Okrusch and Richter, 1969 (X); 91. Papezik, 1965 (S); 92. Patterson, 1951 (S); 93. Patterson, 1953 (S); 94. Patterson and Swaine, 1955 (S); 95. Patterson *et al.*, 1955 (S); 96. Peck *et al.*, 1966 (S); 97. Pecora, 1962 (S); 98. Pinson *et al.*, 1953 (S); 99. Prinz, 1964 (S); 100. Read and Haq, 1963 (S); 101. Read *et al.*, 1965 (X); 102. Renfrew *et al.*, 1966 (S); 103. Renfrew *et al.*, 1968 (S); 104. Ridley, 1970 (S, X); 105. Russell *et al.*, 1954 (S); 106. Sahama, 1945 (S); 107. Savelli, 1967 (X); 108. Shelton, 1955; 109. Siedner, 1965 (S); 110. Siegers *et al.*, 1969 (X); 111. Simpson, 1954 (S); 112. Sinha and Tiwari, 1964 (S); 113. Sinha and Karkare, 1964a (S); 114. Sinha and Karkare, 1964b (S); 115. Smith, 1964 (S); 116. Smith and Carmichael, 1969 (X); 117. Snavely jr. *et al.*, 1968 (S); 118. Staritsin, 1964 (S); 119. Stark and Tracey, 1963 (S); 120. Taylor and White, 1966 (S); 121. Taylor *et al.*, 1968 (S); 122. Taylor *et al.*, 1969 (S); 123. Temple and Grogan, 1965 (X); 124. Townend, 1966 (S); 125. Vlasov *et al.*, 1966 (S); 126. Volborth, 1962 (W); 127. Wager and Mitchell, 1951 (S); 128. Wager and Mitchell, 1953 (S); 129. Wedepohl, 1954 (S); 130. Wedepohl, 1961 (S); 131. Weidel, 1960 (S); 132. Wilkinson, 1959 (S); 133. Wilkinson, 1968.

Differences in Ba concentration among tholeiitic basalts of particular regions were found in South Africa, where Rhodesian tholeiites show unusually high mean Ba values upto 1,020 ppm (Cox *et al.*, 1967), while the basalts of Basutoland and Swaziland are of normal tholeiitic geochemistry. Greenland and Lovering (1966) studied differentiation within a tholeiitic sill in Tasmania (Australia). Ba concentrations increase here, from the bottom to the 1735 ft-high top of the flow, from 160 to 500 ppm. Elements with similar enrichment trends are F and Ga, whereas nonparallel behavior was found for Ni, Co, Cr and Sc.

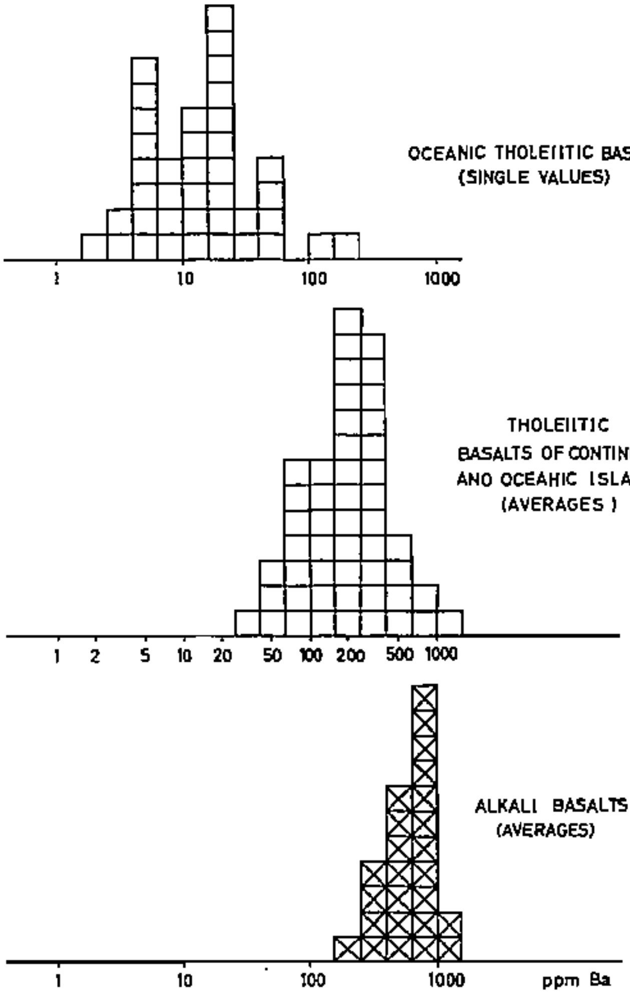

Fig. 56-E-1. Barium distribution in basaltic rocks

Engel *et al.* (1965) gave the ratio of the masses of alkali olivine basalts to tholeiitic basalts as 2:98. Consequently, an average of 253 ppm Ba is to be assumed for average continental basaltic rock. Prinz (1967), in his summary of trace element data for basalts, found an arithmetic mean for all basalts of 303 ppm and a geometric mean of 220 ppm for 253 analyses. From the wide range of Ba concentrations within similar petrographic types and from similar Ba values for different petrographic types within any region, it is indicated that differences in the initial abundance of Ba in basaltic magmas exist (Prinz, 1967). The generation of such differences is attributed to different degrees of partial melting, mantle inhomogeneity or wall rock reactions (Jamieson and Clarke, 1970).

Anorthosites and norites are both lower in Ba than tholeiitic basalts. The normally observed relationship between K and Ba is not found in Canadian anorthosites. In these rocks, which are rich in Ca, the Ba-Ca diadochy is superimposed on the more common Ba-K relation.

III. Granitic Rocks

a) High Ca Content

Granitic rocks with a high Ca content, as in granodiorites and quartz-diorites, are usually high in Ba. Averages are 888 ppm and 811 ppm, respectively; within particular areas the Ba content may vary considerably. An average for both rock types, calculated with the percentages of WEDEPOHL (1969), is 873 ppm.

b) Low Ca Content

Granitic rocks with low Ca content, which are represented by granites and quartzmonzonites, show extremely different Ba values (Fig. 56-E-2). This may be partly due to origin and to differences in the respective processes of formation. Metasomatical alterations may also have changed the Ba content in some granites (cf. EMMERMANN, 1969). The granite average from 28 regional mean values is 732 ppm. Within certain granite bodies, the Ba concentration may exhibit a narrow spread, while the means are low or high. Gradational change of Ba content was also observed (EMMERMANN, 1969). For three quartzmonzonite areas, an average of 1,605 ppm was calculated.

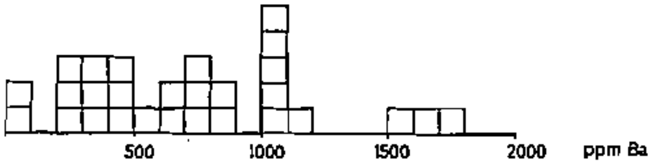

Fig. 56-E-2. Ba distribution in granites (28 local means, see Table 56-E-1)

The effusive equivalents of granitic rocks contain more Ba (average 1,127 ppm) than granites. The single quartz latite value, however, is much lower than the average quartzmonzonite content.

IV. Intermediate Rocks

Intermediate rocks, such as syenites and trachytes, are strongly enriched in Ba. While the syenite average is 2,753 ppm, the effusive equivalent averages only 1,177 ppm. TUREKIAN and WEDEPOHL (1961) gave a value of 1,600 ppm, which was calculated from data of v. ENGELHARDT (1936) and SAHAMA (1945).

V. Alkalic Rocks

Alkalic rocks are all considerably enriched in Ba. All averages are higher than 1,000 ppm, with nepheline-syenite showing 1,427 ppm, phonolite 1,000 ppm and nepheline-basanite 1,976 ppm Ba. In rocks of the Lovozero alkali massif (USSR), Ba is enriched upto 3,300 ppm (VLASOV *et al.*, 1966). The Kola alkali complex (USSR) contains upto 1,600 ppm Ba in its nepheline-syenites and upto 1,350 ppm Ba in the foyaites (GERASIMOVSKII and BELYAEV, 1963).

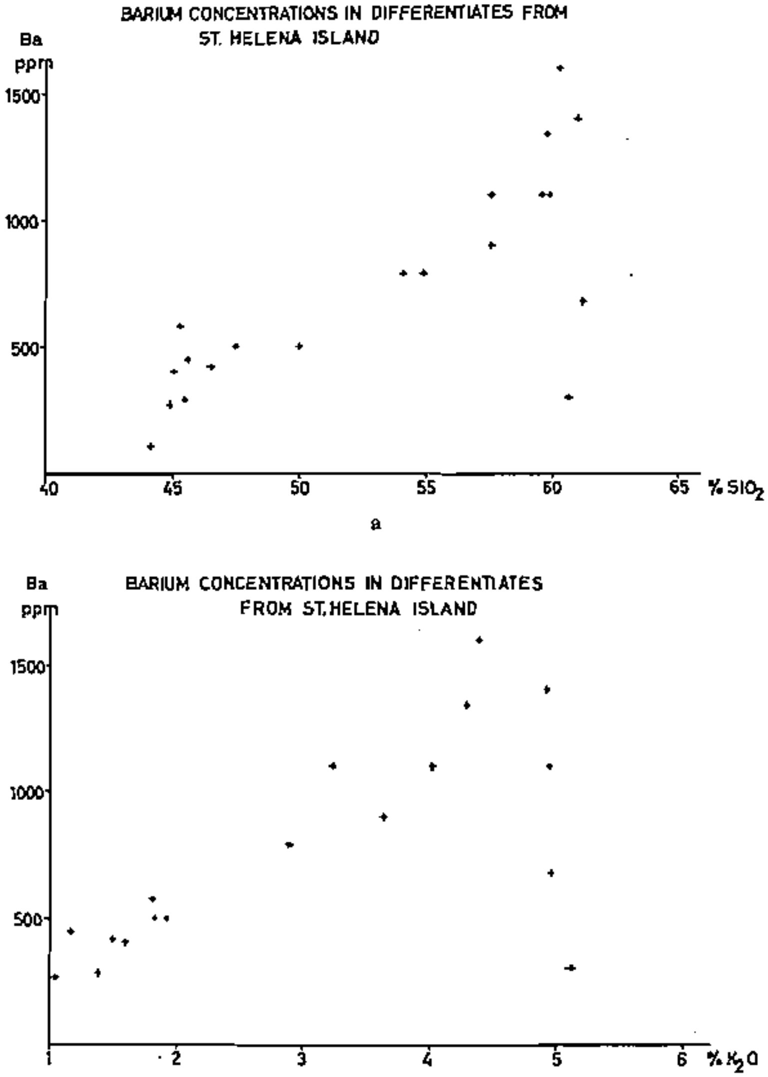

Fig. 56-E-3. Correlation of Ba concentration and SiO_2 (upper plot) and K_2O content in a differentiation series (Baker, 1969)

Many investigators (v. Engelhardt, 1936; Wager and Mitchell, 1951; Nockolds and Allen, 1953, 1954, 1956; Wilkinson, 1959; Markhinin *et al.*, 1964; P. E. Baker, 1968) found that Ba concentrations increase during progressing differentiation. One example of correlation between concentrations of Ba and SiO_2 and K_2O (as parameter of differentiation) is given for volcanic rocks of Saint Helena island, South Atlantic (Fig. 56-E-3).

Sometimes Sr shows the same trend, while a nonparallel behavior is observed for Ca, V, Cu, Co, Ni, and Sc. In several instances the relation between Ba and other elements is not as simple; plotting versus differentiation, solidification, mafic index or Larsen factor provides a better insight into differentiation behavior.

In series which proceed far in differentiation, Ba concentrations normally pass a maximum. Since Ba substitutes mostly for K, this indicates that a distribution coefficient $\left(\frac{\mathrm{Ba}}{\mathrm{K}}\right)_{\mathrm{crystal}} \Big/ \left(\frac{\mathrm{Ba}}{\mathrm{K}}\right)_{\mathrm{melt}}$, larger than unity is effective in acid magmas for at least one major mineral — mostly potash feldspar or mica.

This type of Ba distribution prevails in the example given in Fig. 56-E-3, in the Scottish Caledonian rocks, and the East Central Sierra Nevada rocks analyzed by Nockolds and Allen (1953). As a consequence of this differentiation behavior, Ba is always very low in pegmatites of truly magmatic origin (cf. Table 56-D-1 and v. Engelhardt, 1936). A trend of K/Ba ratios to increase from 26 to 36 in a tholeiitic sequence was found by Gunn (1965).

Data for averages of Ba concentration in igneous rocks have been subject to changes in the last year due to the fact that more and better data have been published. Consequently, the mean calculated Ba content in igneous crustal rocks has changed, since better insight into the relative abundance of rock types was obtained. With the Ba concentrations of Table 56-E-1, one arrives at a Ba average of 728 ppm for the upper continental crust of the earth, using the data for the relative amounts of intrusive rocks by Wedepohl (1969, handbook; Tables 7—8). Examples for Ba distribution between minerals of certain rocks are given in Table 56-E-3.

Compilation and interpretation of Ba data from literature suffer somewhat from the difficulties in analytical determination. This is shown graphically by the Ba values for the standard rocks G1 and W1 (Fig. 56-E-4). The considerable spread of values — even with the same analytical method — cannot be explained by too coarse grain size of the reference samples (Kleemann, 1967), since similar observations were made with the much more finely ground new standard rocks of the USGS (Flanagan, 1969). As the individual authors use their own different values for internal reference, difficulties arise when results from different sources are compared. This must be considered when the data from these paragraphs are evaluated.

Table 56-E-3. *Barium distribution*

Rock type	Total rock Ba ppm	Quartz Ba ppm	Ortho-clase Ba ppm	Plagio-clase Ba ppm	Biotite Ba ppm
Hortonolite ferro gabbro	50			200	
Olivine norite	5			10	
Quartz biotite norite	300			110[a]	1,600
Granodiorite	1,000		3,000	90[a]	2,500
Granite	1,000		2,500	125[a]	2,000
Predazzo granite	70		108	65	100
Adamellite porphyrite	600			275	1,250
Adamellite	110		225		120
Sphen pyroxenite	500	100	900		
Teschenite	275			350	

[a] Quartz and plagioclase.

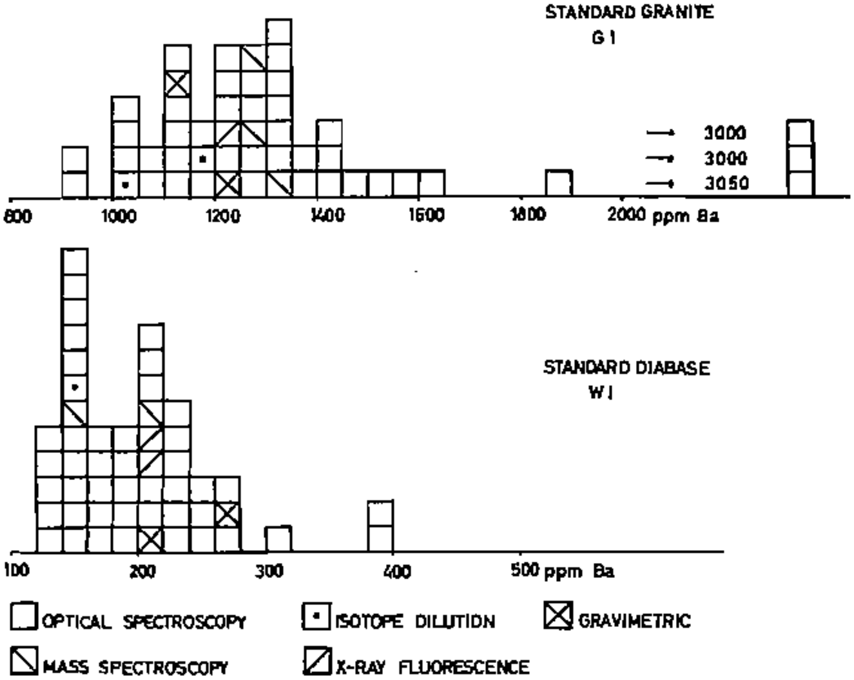

Fig. 56-E-4. Ba determinations on standard rocks (Fairbairn *et al.*, 1951; Stevens *et al.*, 1960; Fleischer and Stevens, 1962; Fleischer, 1965, 1969; Flanagan, 1969)

in rocks

Muskovite	Amphibole	Pyroxene	Olivine	Method	References
Ba ppm		Ba ppm	Ba ppm		
		10	10	S	Wager and Mitchell (1951)
	15			S	Sen *et al.* (1959)
	5	5		S	Sen *et al.* (1959)
				S	Sen *et al.* (1959)
				S	Sen *et al.* (1959)
				S	Emiliani and Vespignani (1964)
	120	35			Wilkinson *et al.* (1964)
10				S	Butler (1953a)
		20		S	Erickson and Blade (1963)
		10		S	Wilkinson (1959)

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56-F. Behavior during Processes Connected with Magmatism

I. Pegmatites

Pegmatites of magmatic origin generally contain less Ba than their embedding wallrocks of magmatic or metamorphic origin. This feature is most apparent in the main Ba carriers, feldspar and mica. By analytical studies of alkali feldspars from the South Norwegian Precambrian basement complex, HEIER and TAYLOR (1959) found that the concentration of Ba in potash feldspars decreases with increasing differentiation. The K feldspars of large pegmatites in the surveyed area always contain less Ba than the host rock. This general trend was diagramatically shown by HEIER (1962) and can also be seen in Fig. 56-D-2, for which additional analyses were used. TAYLOR and HEIER (1960) stressed the importance of the Ba/Rb ratio in feldspars for judging the degree of fractionation. Since Rb is more discriminated against in the K feldspar structure than Ba, Rb is continuously enriched in the fluid during crystallization. Under the assumption of constant distribution coefficients for both elements, this leads to the highest Rb values in the last crystallization. Low Ba values in granite-pegmatite feldspars are also reported by v. ENGELHARDT (1936), OFTEDAL (1958), and TAKUBO and TATEKAWA (1954). Within a pegmatite body, OFTEDAL (1959) found the younger microcline to be poorer in Ba than the older one. Similar Ba impoverishment was found in nepheline-syenite pegmatites (v. ENGELHARDT, 1936; OFTEDAL, 1962) as compared to the lardalite and larvikite from which they are supposed to be derived. Biotite from granite pegmatite also is impoverished in Ba compared to the biotite from the mother granite (TAKUBO and TATEKAWA, 1954).

Ba behavior is different in the small pegmatite bodies which sometimes form by metamorphic processes. In the plagioclase gneiss area of Justøy, Norway, small pegmatitic veins occur with high Ba values. HITCHON (1960) investigated pegmatites of three metamorphic complexes in Scotland. While two complexes showed the usual Ba relation between pegmatite and country rock, pegmatites of the third complex (Laxfordian) were markedly enriched in Ba in all minerals (microcline-perthite 3,785 and 5,620 ppm; oligoclase 365 ppm; biotite 900 ppm, 760 ppm, 1,100 ppm and 2,320 ppm Ba). In these pegmatites, the Ba content of the individual minerals increases towards the core of the respective body. It is possible that in the case of Laxfordian pegmatites metasomatic processes caused a later Ba enrichment in the pegmatite minerals.

II. Metasomatism, Wallrock Alteration, Greisenization

Metasomatic changes of Ba content of rocks occur sometimes with emplacement of pegmatites. Evidence for a large scale metasomatic Ba addition in a rock body was found for the Albtal granite, Germany, by Emmermann (1968, 1969). This author investigated the distinct differences in the distribution patterns of Ba in the two occurring K feldspar generations and reached the conclusion that the potash feldspar megacrysts (mean Ba content 4,600 ppm) had grown during a postmagmatic stage from a metasomatic, Ba rich fluid, whereas the groundmass K feldspar (mean Ba content 1,600 ppm) represents the first generation.

Metasomatic alterations in granodiorite, dacite, and gabbro related to serpentinization of ultramafic rocks in the Western United States, generally resulted in a distinct Ba impoverishment. In a few cases, small intermediate zones with Ba enrichment were observed (Coleman, 1967).

Lur'ye (1963), analyzing spectrographically the silicic wallrocks of Zambarah zinc-lead ore deposit, Central Asia, found a pronounced decrease in the concentration of Ba and Sr towards the veins. The Ba content drops from 3,000 to 6,000 ppm, in fresh rock containing abundant K feldspar, to 300 ppm as a maximum in completely sericitized, feldspar free rocks close to the ore. He concludes that all barite and its Sr content originates from the feldspar decomposition in the wall rocks. Granitic wallrocks of hydrothermal veins in the Black Forest, Germany, were analysed for Ba distribution by Degens (1956). Extensive studies of wallrock alterations were carried out by Tooker (1963) in the Front Range Mineral Belt, Colorado, USA. His spectrographic analyses showed that Ba, as with other large ions, normally tends to be removed veinward from all Precambrian and Tertiary metamorphic and igneous rocks he investigated. During alteration in the rock, pH drops along with the decrease of K, Ba etc.

Greisenization normally proceeds with the removal of Ba from the affected rock. In a mixture of samples from 24 greisen, v. Engelhardt (1936) found an abundance of 160 ppm Ba. This value is far below the content in the respective unaltered igneous silicic rocks. Solomon (1966) reports Ba removal from granites (430 ppm and 250 ppm) by greisenization (Ba in the altered rocks: 160 ppm and 105 ppm respectively) in the North Pennine ore field, Great Britain.

III. Ore Deposition

Probably, magmatic-hydrothermal fluids originally do not contain any significant amount of Ba, but obtain this element by leaching suitable wallrocks. The importance of this mechanism, mentioned in the previous paragraph, was already stressed by v. Engelhardt (1936). Another mechanism working in sedimentary environments is dissolution of barite from the sediment by bacterial sulfate reduction in suitable diagenetic environment (Puchelt, 1967). As a third way of producing Ba containing fluids, certain metamorphic reactions may give off Ba because structures which had incorporated high Ba concentrations become unstable.

The most common Ba ore is barite. It is deposited by fluids with a high oxidation potential, where sulfur is present as sulfate. Suitable conditions of this kind occur close to the earth's surface or in subsurface areas where sulfate solutions mix with reduced Ba containing waters (cf. Subsection 56-I-IV). In solution, Ba migrates to the region of sulfate stability and thus is often bound to a narrow zone close to the earth's surface.

Modes of barite formation and possibilities of $BaSO_4$ transport in solution are discussed by PUCHELT (1967). Barite contains, in all cases, certain amounts of isomorphous Sr. Concentrations of this element in marine barites (upto 3.36%) are summarized by CHURCH (1970). STARKE (1964) analysed a large number of vein barites which contain upto 12% $SrSO_4$. The conditions necessary for witherite formation from ore forming fluids are not often fulfilled. Calculations for $BaCO_3$ formation, at 250° C and CO_2 fugacities of 0.1, 1.0 and 100 atm., were carried out by HOLLAND (1965) for varying sulfur and oxygen fugacities.

Products of hydrothermal activities are also the alpine fissure type minerals of which adularia are sometimes most apparently enriched in Ba (cf. Table 56-D-1).

IV. Volcanic Exhalations, Gas Transport

The possibility of Ba transport through hydrous gas phases was demonstrated by the experiments of STRÜBEL (1967). Results are discussed in chapter 56-H. NABOKO (1945) found traces of Ba in fumarole sublimates (mostly NaCl, KCl and NH_4Cl) of Klyuchevskoy volcano, USSR. MINGUZZI (1948) determined traces of Ba in fumarole products of Vesuvius, Italy.

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56-G. Behavior during Weathering and Alteration of Rocks

Experimental weathering of K feldspar in distilled water (Puchelt, 1967) showed that Ba is preferentially released from this silicate structure into the solution. The weight ratio K_2O/BaO, being 18.9 in the mineral, is much lower in the weathering solution (8.1).

In the naturally occurring weathering series biotite — hydrobiotite — vermiculite, Boettcher (1966) observed, by spectrographic analysis, a decrease of the BaO content from 4,500 ppm to 300 ppm.

Rosenquist (1939) leached a granite powder (0.11% BaO) with distilled water. In the residue of the weathering solution BaO was enriched to 0.91%.

Extensive studies on different rocks and their weathering products were carried out by Butler (1953b, 1954) (Table 56-G-1). In three types, Ba is enriched in the silt and clay fraction of the weathered material, while in a fourth example even the weathering residue is leached with respect to Ba.

Table 56-G-1. *Barium distribution during rock weathering* (Butler, 1953b, 1954)

Rock type	Ba content (ppm)			Reference (Analytical method)
	fresh rock	from weathered rock		
		silt fraction	Ca saturated clay fraction	
Granite	110	180	500	Butler, 1953b (S)
Hornblende schist	10	190	500	Butler, 1953b (S)
Quartz free syenite	1,000	300	870	Butler, 1954 (S)
Hypersthene monzonite	1,000	45	15	Butler, 1954 (S)

Both Ba increase and Ba decrease have been observed in the weathering products in studies by a great number of investigators. Among the factors which influence Ba behavior in this process are: climate; type of clay minerals, which form during the decomposition; amount and kind of organic material present; and sulfur or sulfate content. Since barium sulfate is a compound of very low solubility, this last factor predominates in sequences originally rich in sulfides.

A survey of Ba content of soils was published by Swaine (1955). Most soils contain 100 to 3,000 ppm Ba of which only trace amounts can normally be extracted by means of 1N NH_4 acetate. The highest value which Swaine reports (3.3% Ba) comes from Tennessee, USA, from areas where barite had been mined. Older literature is listed in Gmelin (1960). Under special arid conditions of weathering in deserts, varnishes form, which always show Ba enrichment (Engel and Sharp, 1958) (S).

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56-H. Solubilities of Compounds which Control Concentrations of Barium in Natural Waters (I), Adsorption Processes (II)

I. Solubilities

Only two Ba compounds exist which can control the Ba content of natural waters: $BaSO_4$ — barite, and $BaCO_3$ — witherite.

a) Solubility of $BaSO_4$

$BaSO_4$ is the least soluble and most abundant Ba mineral in the earth's crust. Its solubility in water upto 100°C has been repeatedly determined. Some of the available data are given in Fig. 56-H-1. **Strübel** (1967) published data for $BaSO_4$ solubility in the hydrothermal range upto 600°C. At this temperature and 1,084 bars, he obtained a solubility of 9.61 ± 1.95 mg $BaSO_4$/1,000 g H_2O.

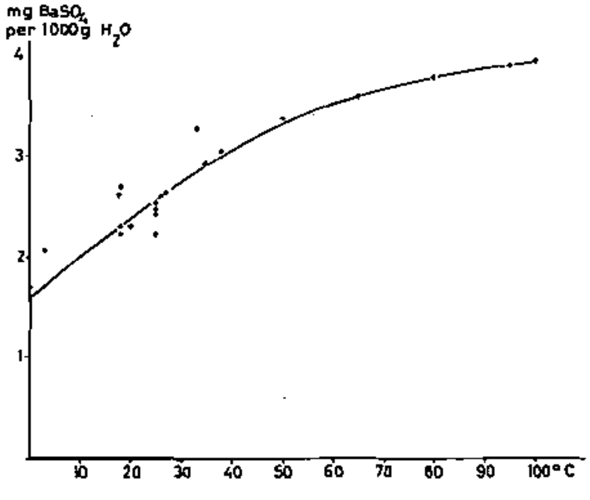

Fig. 56-H-1. Solubility of barium sulfate in distilled water (**Kohlrausch**, 1908; **Melcher**, 1910; **Neumann**, 1933; **Rosseinskt**, 1958; **Templeton**, 1960; **Burton** *et al.*, 1968)

Electrolytes considerably increase the $BaSO_4$ solubility. **Templeton** (1960) has investigated sodium chloride influence upto 95°C with solutions upto 5 molal NaCl. **Puchelt** (1967) radiochemically determined $BaSO_4$ solubility at 25 and 50°C in upto 6.08 molal NaCl solutions. Experiments upto 350°C were carried out by **Uchameyshvili** *et al.* (1966) with 0.25 N, 1.0 N and 2.0 N sodium chloride solutions. Investigations upto 600°C with upto 2 molal (or 11.69% ?) NaCl solutions were performed by Strübel (1967). Solubility data upto the boiling point are plotted versus NaCl molality in Fig. 56-H-2. For 600° C, 1,990 bars and 2N (?) NaCl solutions, Strübel reports a solubility of 971 mg/kg H_2O. In the hydrothermal range, $BaSO_4$ solubility sensitively increases with pressure. Strübel's investigations show that an area of retrograde $BaSO_4$ solubility exists between 350 and 450°C.

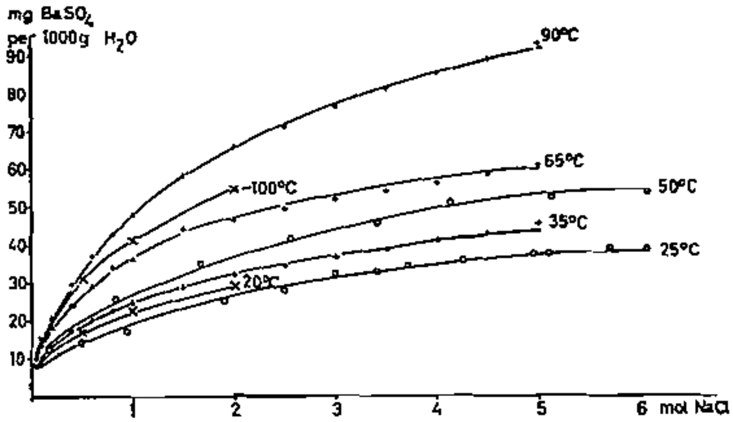

Fig. 56-H-2. Solubility of barium sulfate in NaCl solution. + Templeton, 1960; × Strübel, 1967; o Puchelt, 1967

Influences of other electrolytes on $BaSO_4$ solubility in aqueous solutions were studied by: Neumann (1933), KCl, KNO_3, $MgCl_2$, $Mg(NO_3)_2$, $LaCl_3$, $La(NO_3)_3$; Uchameishvili *et al.* (1966), KCl, $MgCl_2$, $CaCl_2$; and Puchelt (1967), KCl, $MgCl_2$, $CaCl_2$. Collins and Zelinski (1966) investigated the effect of synthetic brines containing NaCl, $MgCl_2$, $CaCl_2$, and $NaHCO_3^-$.

The results of Puchelt are:

Solution	Maximum solubility found at		$BaSO_4$ solubility mg/1,000 g H_2O
	temperature	ionic strength	
KCl	25° C	5.0	40.8
KCl	50° C	5.0	54.0
$CaCl_2$	25° C	5.5	42.4
$CaCl_2$	50° C	5.5	59.8
$MgCl_2$	25° C	6.0	47.2
$MgCl_2$	50° C	6.0	71.6

Uchameishvili *et al.* (1966) found a strong increase in $BaSO_4$ solubility in $CaCl_2$ solutions with temperatures between 100 and 255°C. In $MgCl_2$ solutions, too, a barium sulfate solubility higher than that in NaCl and KCl solutions was observed by these investigators.

Barium sulfate solubility in sea water was calculated by Chow and Goldberg (1960), and experimentally studied at one atmosphere pressure by Puchelt (1967), who also made investigations regarding the kinetics of $BaSO_4$ precipitation in sea water. The solubility of 89 μg $BaSO_4$/l (at 20° C), found by **Puchelt** agrees well with the value of 87.9 μg $BaSO_4$/l (at 25° C) of **Chow** and **Goldberg**. Recently, **Burton** *et al.* (1968) obtained a mean value of 81 μg/l. Close to saturation, complete equilibrium is reached slowly. Despite seeding, **Puchelt** (1967) needed about 80 days. He also made experiments to study the influence of salinity of sea water on solubility and covered the range upto $87.5\,^0/_{00}$ salinity. **Hanor** (1969) and **Church** (1970) calculated the effect of aqueous complexing and presence of Sr, Ca, and K on the solubility of $BaSO_4$—$SrSO_4$ mixed crystals in sea water.

Pressure increases the solubility of $BaSO_4$. In pure water the solubility product is, by a factor of 5.4, larger at 1 kilobar than at 1 atm. pressure. In a sodium chloride solution of 0.727 molality the same ratio is only 4.2.

b) Solubility of $BaCO_3$

Barium carbonate solubility depends largely on the CO_2 partial pressure of equilibrium atmosphere. At 25° C and 1 atm. CO_2 pressure, **Garrels** *et al.* (1960) determined a dissociation constant of $10^{-8.84}$ for witherite. The solubility product of ^{14}C-labeled $BaCO_3$ in basic aqueous solutions at 25° C was found to be $4.0 \cdot 10^{-10} \pm 0.5 \cdot 10^{-10}$ by **Baccanari** *et al.* (1968).

Increase in carbon dioxide pressure causes an increase in $BaCO_3$ solubility. This effect is much smaller at higher temperatures than at lower temperature (**Malinin**, 1963), (Fig. 56-H-3).

Townley *et al.* (1937) showed that LiCl, NaCl, and KCl at 25° C and 40° C, increased $BaCO_3$ solubility according to their respective concentration. In all concentrations investigated (upto 3 molal) LiCl produced the strongest increase in solubility. The effect of KCl in the same molality was the least.

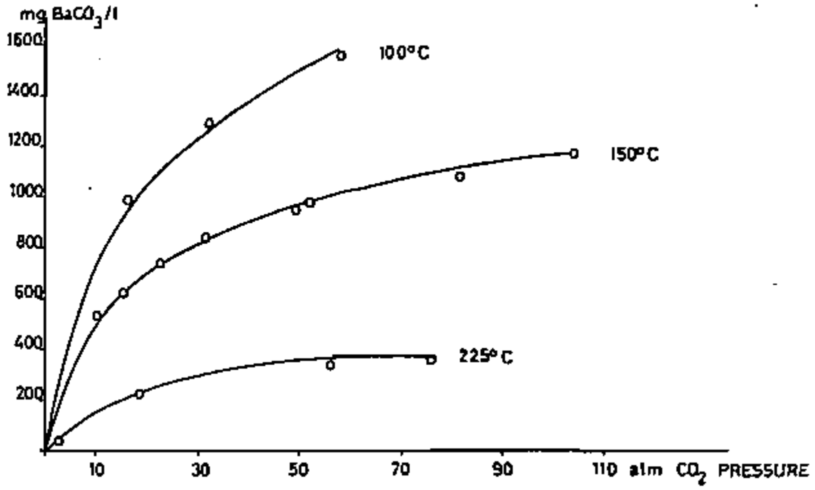

Fig. 56-H-3. Solubility of $BaCO_3$ in water with increasing CO_2 pressure (**Malinin**, 1963)

II. Adsorption Processes

Ba is adsorbed from solutions by clays, hydroxides, and organic matter. In addition to $BaSO_4$ solubility, these processes control the amount of Ba present in natural waters.

a) Clays

Ba adsorption on the sodium charged form of standard montmorillonite, illite, and kaolinite, at 25°C was studied by Puchelt (1967) for pure and electrolyte containing solutions. Ba adsorption decreases with ionic strength of the exchange solution. In rivers, the ratio of Ba which is adsorbed by suspended matter depends on the type of suspension and the concentration of ions competing for adsorption sites.

Ba exchange on vermiculite and bentonite was investigated by Levi and Schiewer (1965). Bentonite adsorbs Ba more strongly than NH_4^+, Mg^{++}, and Ca^{++} (Komlev *et al.*, 1965). Carlson and Overstreet (1967) found a high adsorption of incompletely dissociated Ba hydroxide by bentonite at pH 6. The heat of exchange of Ba ions on bentonite with H^+, Na^+, and K^+ were calorimetrically determined by Tadziev and Muksinov (1967). Ganguly and Mukherjee (1951) investigated Ba exchange on bentonite, kaolinite, illite, and mica.

b) Hydroxides

Ba adsorption by hydrous ferric oxide was investigated by Duval and Kurbatov (1952). Puchelt (1967) studied, experimentally, Ba adsorption on γ MnO(OH) and found that NaCl concentrations upto 3.5% do not influence the amount of Ba adsorption. γ MnO(OH) can adsorb as much as 20% (by weight) of its Mn content of Ba. These results probably can explain the Ba content of deep sea manganese nodules. Puchelt also observed that γ MnO(OH) adsorbs more than 85% of the Ba concentration which exists in equilibrium with a $BaSO_4$ precipitate. Adsorption of Ba ions on silica gels from acid solutions depends on time of exchange, specific surface, and pore size of the gel (Kirichenko *et al.*, 1965).

c) Organic Substances

Bel'Kevich *et al.* (1966) equilibrated 0.05 to 0.2N earth alkali solutions with the H-form of peat. They found Ba to have the strongest tendency to substitute for H in peat. Adsorption of ^{137}Ba by coal humic acid was studied by Matsumara and Ishiyama (1966). Puchelt (1967) observed that bacteria may extract Ba from solutions, but it is not yet clear, whether this happens by adsorption or incorporation.

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56-I. Abundance in Natural Waters

I. Springs and Fresh Water Wells

Only very few spring and fresh waters are free of sulfate. Thus the solubility product of $BaSO_4$ is the limiting factor for the Ba concentration. As spring waters normally have only low amounts of dissolved solids and moderate temperatures, no considerable increase of $BaSO_4$ over the distilled water solubility is to be expected. These waters originate normally from rain water which had only a limited time for equilibration in sediments and soils. The Ba content is mainly controlled by the solution of Ba compounds (mostly barite), and exchange of Ba from silicate structures. Several analyses are published for water which served medical purposes. A survey of older data (methods: W) is given by **Delkeskamp** (1900, 1902); some values published before 1949 are tabulated by **Gmelin** (1960). **Puchelt** (1967) surveyed the more recent literature grouping the waters in hydrocarbonate, chloride, sulfide and sulfate types according to their prevailing anion.

Table 56-I-1. *Ba concentrations in European spring waters.* (**Puchelt**, 1967)

Type of water	No. of springs	Ba range ppb	Arith. mean ppb	Standard deviation
Hydrocarbonate	16	4—22,900	1,757	5,672
Chloride	22	12— 9,500	1,340	2,681
Sulfide	3	150— 750		
Sulfate	9	1— 230		

In very few cases of spring water, higher values were observed than were expected from the $BaSO_4$ solubility product. Their existence is explained by supersaturation which sometimes occurs for a short time after adding sulfate to Ba solutions.

Drinking water from fresh water wells was analysed in the USA by **Durfor** and **Becker** (1964). For 10 wells from all parts of the country they found 4.6 to 34 ppb Ba (S).

Additional new data for ground and spring waters were published for: South Africa (**Kent**, 1949; **Kent** and **Russell**, 1949), Bulgaria (**Penchev** *et al.*, 1958, 1960), Czechoslovakia (**Rubeska** and **Miksovsky**, 1963), Finland (**Wilska**, 1952), Germany (**Fricke**, 1968), Hungary (**Straub**, 1950), Japan (**Ikeda**, 1955a/b; **Ichikuni**, 1966; **Iwasaki** *et al.*, 1963), and the Soviet Union (**Babinets** and **Radko**, 1956; **Grushko** and **Shipitsyn**, 1948; **Kontorovich** *et al.*, 1963; **Ostrdumov** and **Russkikh**, 1965; **Shinkarenko**, 1948; **Yusurova**, 1957). The highest value reported comes from a Japanese warm spring of sodium chloride type and is 62 ppm Ba.

II. Rivers and Lakes

Only North American rivers have been extensively analysed for Ba. The investigations of Durum *et al.* (1960) and Durum and Haffty (1961) cover long periods of time, climatic conditions and discharge for a number of rivers. In all cases they found, over a year, a considerable and complex variance of Ba content. One example is given in Table 56-I-2.

Table 56-I-2. *Variation of Ba concentration in Mississippi water near Baton Rouge, Louisiana, U.S.A.*

Date of sampling	Run-off m^3/sec	Dissolved solids ppm	Ba ppb
May 10, 1958	24.550	160	78
Oct. 14, 1958	7.400	223	127
March 13, 1959	18.600	184	72
May 18, 1959	11.800	255	84

Durum *et al.* (1960) covered 30% of the total run-off of the North American rivers with their analyses, and Durum and Haffty (1963) found a median Ba concentration of 45 ppb from the available data. Ba/Sr ratios (by weight) vary between 0.2 and 3.9 (Puchelt, 1967), but give a geometric mean of 0.87 for North American rivers (Durum and Haffty, 1963), which may be compared with $0.78 \cdot 10^{-3}$ in the oceans. A number of rivers and lakes being used as drinking water resources have been analysed for Ba by Durfor and Becker (1964). By spectrographic analyses, they determined a range of Ba content in rivers between 3.1 and 340 ppb (arithmetic mean: 75.7 ppb). Lakes and brackish water in North America and Europe ranged from 3 to 140 ppb Ba (Durfor and Becker, 1964; Brown *et al.*, 1962; Wilska, 1952; Landergren and Manheim, 1963). Concentration ranges for several rivers are plotted in Fig. 56-I-1.

Local variations of Ba content due to rock composition of the drained area were found by Miller (1961) in New Mexico and Brown *et al.* (1962) in Alaska. They observed the highest Ba values from regions with sediments (sandstone, slates), less from granites, and obtained the lowest means from quartzite. The distribution of Ba along a river was studied by Leutwein and Weise (1962) for the Mulde in Germany. They observed values of 5 to 100 ppb Ba in true solution in the river itself but upto 730 ppb in certain adjoining creeks which drained mining areas. According to these authors, in the upper part of the river 70% and more of the Ba is transported in true solution as the ion. On flowing into the Elbe after 245 km, only 20% of the Ba is still in the ionic form, 80% having been adsorbed onto clays and organic matter. In regions with extreme sulfate concentrations, Ba content is low in accord with the $BaSO_4$ solubility product. Turekian *et al.* (1967) describe the Ba variation of the Neuse river (North Carolina, USA). Ba concentration decreases in the upper part of the river, (16 to 5.7 ppb) in slate and granite areas, but increases regularly downstream to 22 ppb in slate, schist, sand and limestone

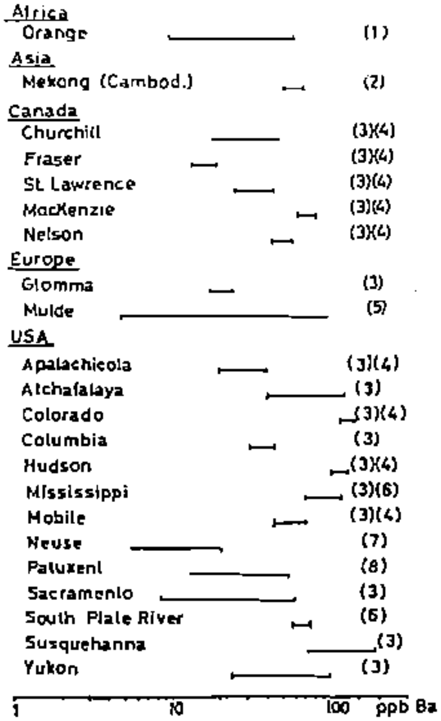

Fig. 56-I-1. Ba concentration ranges of rivers (all data obtained by spectrographic methods). 1. Devilliers (1962); 2. Durum and Haffty (1963); 3. Durum *et al.* (1960); 4. Durum and Haffty (1961); 5. Leutwein and Weise (1962); 6. Durfor and Becker (1964); 7. Turekian *et al.* (1967); 8. Heidel and Frenier (1965)

areas. Where the petrographic composition influences the drainage waters of a certain area distinctly, no general conclusion can be drawn from trace element data from large river basins regarding the origin of the particular trace element.

III. Oceans

From all oceans, Ba determinations are available in surface to bottom profiles. The concentration ranges upto 78 ppb Ba and the estimated mean is about 20 ppb (Turekian and Johnson, 1966). Analytical data are compiled in Table 56-I-3.

In general, the Ba concentration seems to be lower in the Atlantic than in the Pacific. In most cases the surface layers are depleted in Ba. Special features have been observed for the distribution of Ba in the Pacific close to the equator; Chow and Goldberg (1960) have found a steady increase of Ba concentration with depth in the respective profiles (Fig. 56-I-2a). They explained this by high biological activity in the surface layers of this region, incorporation or adsorption on organic matter, and a downward transport with the organic debris. They found Ba to resemble radium in distribution with depth. Wohlgemuth and Broecker (1970) could also correlate Ba content with concentrations of other bio-important elements and found parallels with Ra distribution. These authors sampled from very deep

Table 56-I-3. *Ba concentrations in the oceans*

Locality	Maximum sampling depth (m)	No. of samples	Ba range ppb	Method	References
Pacific Ocean					
Central part, close to equator	4,752	18	10—63	I	Chow and Goldberg (1960)
	4,350	4	19—33	N/R	Turekian and Johnson (1966)
Philippine Sea	4,000	10	11—33		Turekian and Johnson (1966)
Antarctic	5,120	125	8—56		Turekian and Johnson (1966)
South East Pacific	1,500	8	9—17		Turekian and Johnson (1966)
South West Pacific	5,000	5	19—78		Turekian and Johnson (1966)
East Pacific	4,580	13	8.5—31.2	I	Wolgemuth and Broecker (1970)
East Pacific	4,000	13	6.1—23.5	I	Wolgemuth (1970)
Indian Ocean					
Central part	surface	1	14	N/R	Turekian and Johnson (1966)
West Indian Ocean	400	3	21—46		Turekian and Johnson (1966)
South Indian Ocean	4,500	3	10—15	N/R	Bolter *et al.* (1964)
Atlantic Ocean					
Long Island Sound	39	60	9—32 (65)	N/R	Turekian and Johnson (1966)
Caribbean, Gulf of Mexico	3,019	17	5—23		Turekian and Johnson (1966)
South Atlantic	5,000	3	15—21		Turekian and Johnson (1966)
North Atlantic	5,061	21	9—31		Turekian and Johnson (1966)
	4,100	3	12.9—13.1	N/R	Bolter *et al.* (1964)
	3,000	8	12—18	I	Chow and Patterson (1966)
	2,098	16	0.04—22.8	F	Andersen and Hume (1968)
Equatorial	4,387	35	0.80—37.5		Andersen and Hume (1968)
English Channel	surface	1	6.3	N/R	Bowen (1956)
Caribbean	4,729	20	7—23	S	Szabo and Joensuu (1967)
Puerto Rico Trench and off Barbados	7,540	28	7.9—19.1	I	Wolgemuth and Broecker (1970)

ocean regions but did not find a marked Ba increase towards the sea floor. Turekian and Johnson (1966) observed, in some places, a maximum of Ba concentration in depths of 600 to 1,200 m (Fig. 56-I-2b) which, however, coincides with the region of lowest Ba sulfate solubility (35 µg/l) in agreement with the interaction of tem-

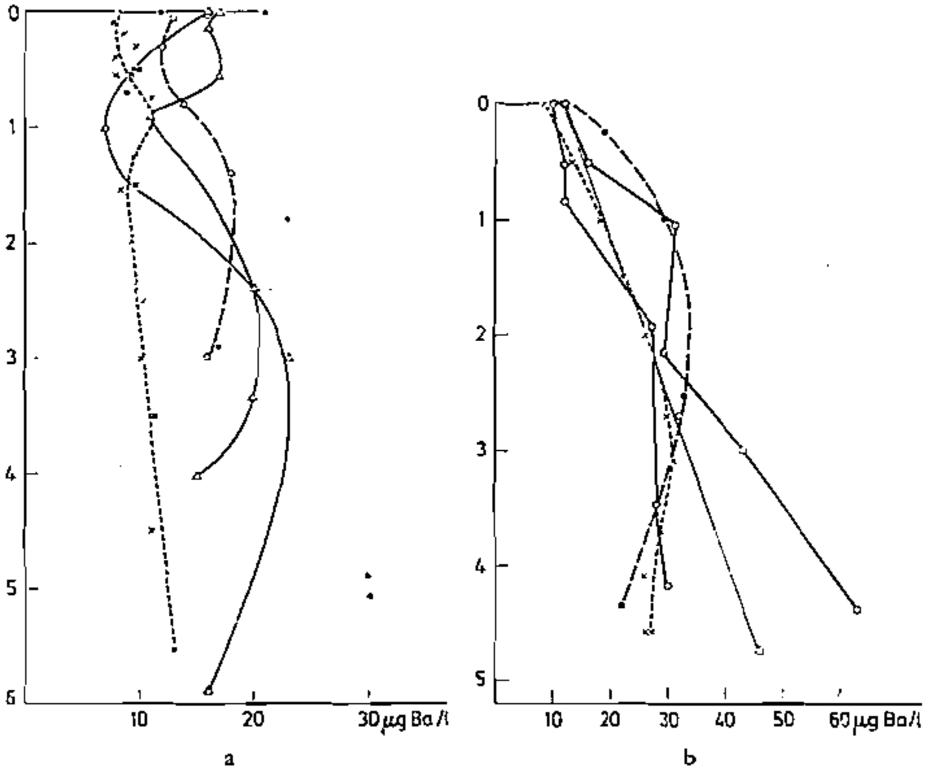

Fig. 56-I-2a and b. Barium distribution in the oceans. a Barium profiles in the Atlantic. × Wolgemuth and Broecker, 1970; o Chow and Patterson, 1966; ● Turekian and Johnson, 1966; Δ Szabo and Joensuu, 1967. b Barium profiles in the Pacific. × Wolgemuth and Broecker, 1970; o Chow and Goldberg, 1960; Turekian and Johnson, 1966

perature decrease and pressure increase (Chow and Goldberg, 1960). One possible explanation for these high values could be that microcrystals of barite have contaminated the samples. Szabo and Joensuu (1967) found in profiles in the Caribbean the lowest concentration in the depths of about 1,000 m (Fig. 56-I-2a). In two areas, the equatorial Pacific and the Atlantic off southwest Africa, high values for Ba were found both in the sediments and in sea water, whereas in other places no correlation could be detected.

From the Ba supply of the streams, saturation of Ba sulfate should almost be reached in the oceans. From stream discharge ($3.6 \cdot 10^4$ km^3/yr) and Ba concentration of 45 ppb (Durum and Haffty, 1963), ocean-mass of $1{,}372 \cdot 10^6$ km^3, and Ba content of 20 µg/l (Turekian and Johnson, 1966), the residence time of Ba in the sea can be calculated to be $17 \cdot 10^3$ years. Using a sedimentation rate of 0.05 g SiO_2/yr for diatomaceous ooze (based on ^{32}Si), a Ba content of 6,000 ppm and a mean ocean depth of 5,000 m, Turekian and Johnson computed a residence time of only 33 years above this particular sediment. Possibly this low value and the observed increase of Ba content with depth indicate an additional supply of Ba from some volcanic source on the ocean floor. With an average of 20 µg/l Ba, the total content of the oceans is $27.4 \cdot 10^9$ tons of Ba.

Table 56-I-4. *Barium concentration in formation waters*

Period	Country	Total No. of samples	No. of samples >1 ppm Ba	Mean Ba conc. of samples with Ba >1 ppm	Maximum Ba conc. ppm	Analytical method	Reference
Precambrian	U.S.A.	1	1	4	4	S	White (1965)
Ordovician	U.S.A.	4	3	61	100	S	McGrain and Thomas (1951)
Silurian	U.S.A.		1	320	320	S	McGrain and Thomas (1951)
Devonian	Canada		2	2	2	S	White (1965)
	Germany	2	1		1.1	W	Fresenius (see Michel 1963)
	U.S.A.	37	21	218	1,140	S	Poth (1962)
		13	7	205	700	W, S	Price *et al.* (1937), White *et al.* (1963)
		69	12	828	2,000	S	Hoskins (1947)
	U.S.S.R.	73	67		971	S	Kozin (1964)
Carboniferous (Mississippian, (Pennsylvanian)	Belgium	1	1	347	347	S	Camerman (1951)
	Germany	4	3	1,007	1,260	S	Jakobshagen and Münnich (1964)
		249	46	1,006	2,860	W	Michel (1963)
		225	69	832	2,806	W, S	Puchelt (1964), (1967)
		152	38	798	2,000	W, S	*Wasserwirtschaftsstelle* (in Puchelt, 1967)
	Great Britain	38	22		5,100		Anderson (1945), Gibson (1963)
	U.S.A.	152	112	447	5,530	W, S	Price *et al.* (1937)
		77	34	265	1,080	S	Poth (1962), Hoskins (1947)
		72			600		Collins (1969)
		36	20	236	1,980	S	McGrain and Thomas (1951)
	U.S.S.R.	111	≧36		190	S	Kozin (1964)
Permian	Germany		4	11	21	S	Herrmann (1961)
	U.S.A.		3	5.2	9.6	S	White *et al.* (1963)
	U.S.S.R.	48	≧5		73	S	Kozin (1964)
Jurassic	Germany	26	7	14.8	30	S, W	Puchelt (1967)
Cretaceous	Sweden	8	2	1	1	S	Assarson (1948)
	U.S.A.		24	14	72		Buckley *et al.* (1958), White *et al.* (1963)
Tertiary	Japan	3	1	59	59	S	Bailey *et al.* (1961)
	U.S.A.		15	37	150	S	Bailey *et al.* (1961), White (1965)
Quarternary	Poland	6	2	3.6	4		Dowgiallo (1965)
	U.S.A.	2	2	16	28	S	White *et al.* (1963)

IV. Formation Waters

Frequently, Ba was discovered in formation waters which had lost their initial sulfate content through bacterial activity during diagenesis. As these bacteria require a reducing environment and organic substances to live on, their areas of activity and thus high Ba concentrations in formation waters, are always connected with occurences of organic matter (oil, bitumen, coal, or gas). Ba has been found in such waters from beds of all geological ages from all over the world. The Ba concentration may reach 5,500 ppm, but no correlation of the Ba concentration with any other parameter of the solutions (dissolved solids, Sr, Ca, K concentration) could be found. Often the Ba/Sr weight ratio is larger than unity. An extensive survey of data is given by PUCHELT (1967). A more condensed compilation was prepared for this chapter (Table 56-I-4).

In the Soviet Union, Ba concentrations in formation waters have been successfully used for a correlation of stratigraphic horizons (KOZIN, 1964; NIKOLAEV *et al.*, 1960). Ba has been assayed in formation waters of a few areas, especially in connection with oil field investigations (AKHUNDOV and SAPPO, 1960; DODONOV *et al.*, 1949; KATCHENKO and FLEGONTOVA, 1955, 1956; KAVEEV and VASIL'EV, 1956; KOROLEV, 1938; KUKABAEV and SYDYKOV, 1962; SKROBOV and SMIRNOV, 1939; SUKHAREV, 1961; TIMASHEVA, 1963; VAROV and ROMM, 1942).

Mixing of Ba-containing formation waters with sulfate waters is often the reason for a scale formation in oil wells (GATES and CARAWAY, 1965; TEMPLETON, 1960) and mines (PATTEISKY, 1954; ANDERSON, 1945). PUCHELT (1967) presented evidence for the abundant formation of certain types of barite deposits from those waters.

V. Brines

Geothermal brines were tapped by deep wells near the Salton Sea, California, USA, an area characterized by rhyolites and Tertiary sediments. With a total of 319,000 ppm evaporation residue (180° C), 200 ppm Ba were reported for a 1963 sample (WHITE, 1965) whereas 1966 samples from two wells gave 235 and 250 ppm Ba (SKINNER *et al.*, 1967). A hot brine from the Atlantis II Deep in the Red Sea containing more than 300 g dissolved solids per liter had almost 1,100 ppb Ba (MILLER *et al.*, 1966).

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56-K. Abundance in Common Sediments and Sedimentary Rock Types

A compilation of data on the Ba distribution in recent and fossil sediments has been published by PUCHELT (1967). An abbreviated review, but with the important new data included, is given below.

I. Recent Sediments

a) Deep Sea Sediments

Deep sea clays were often analysed for Ba in recent years. Generally, they are enriched in Ba compared to shales. WEDEPOHL (1960) found a definite difference between Atlantic clays (average: 750 ppm Ba) and Pacific clays (average: 4,000 ppm Ba). Since the rate of Ba deposition is about the same in both oceans, he assumed the difference to be caused by a lower rate of detrital accumulation in the Pacific. GOLDBERG and ARRHENIUS (1958) found Ba enrichment in sediments under equatorial waters and related this observation to the high biological productivity in the surface layers of the waters. Several planktonic organisms are known to accumulate Ba in their tests which carry the Ba bottomward after death. They may cause a Ba enrichment in layers close to the bottom, where they dissolve, and may generate local $BaSO_4$ precipitations (PUCHELT, 1967; BRONGERSMA-SANDERS, 1967; cf. Table 56-L-2). Barium is not deposited homogeneously on the sea floor. The zones of high biological activity as well as the ocean ridge systems usually have higher Ba concentrations (TUREKIAN, 1968) than normal deep sea sediments. The origin of Ba in deep sea sediments is a matter of discussion.

BOSTRÖM and PETERSON (1966) determined upto 3.1% Ba in cores from the flanks of the East Pacific Rise. From additional data for other elements and data for the heat flow, it can be concluded that volcanic activity adds several of the enriched elements. TUREKIAN (1968) concluded from data of Ba supply to the oceans by streams, from average Ba content of clays (shales), from the model of Ba enrichment by plankton and from some additional information, that a volcanic or hydrothermal Ba supply need not be assumed to explain the observed Ba data. Ba concentrations in deep sea matter do not often correlate with any of the major constituents. It has to be concluded that Ba adsorption on clays is of less importance. The main Ba carrier is most likely barite. Locally, manganese oxides and phillipsite will accumulate Ba. Calcium carbonate of organic origin is usually very low in Ba (<100 ppm, often only 10 to 30 ppm). In order to reach comparable data for clay sediments, TUREKIAN and TAUSCH (1964) have calculated their Ba determination of Atlantic cores on calcium carbonate free basis. Because the original data are not given, only these corrected values are included in Table 56-K-1. These authors found higher Ba values in the South Atlantic than in the North Atlantic. The areas

Table 56-K-1. *Ba concentrations in deep sea sediments*

Origin	No. of samples	Ba content ppm	Method	References
		a) Deep sea clays		
Atlantic				
Area north of equator	1	200	S	v. Engelhardt (1936)
South Atlantic	2	590	S	v. Engelhardt (1936)
Area north of 20° S	37	596[a]	S	Ericson *et al.* (1961)
Area north of 10° N	62	1,100[a]	S	Turekian and Tausch (1964)
Area south of 10° N	63	2,000[a]	S	Turekian and Tausch (1964)
Area north of equator	5	910	S	El Wakeel and Riley (1961a)
North American trench, south part	15	725	X	Wedepohl (1960)
Kap Verde Trench	3	470	X	Wedepohl (1960)
Mid Atlantic Ridge	1 (9)	4,400[c]	N/R	Turekian (1968)
Average of Atlantic clays	189	1,260		
Pacific and Indian Ocean				
Area south of equator	8	1,150	S	Goldberg and Arrhenius (1958)
Area north of equator	5	5,700	S	Goldberg and Arrhenius (1958)
Baja Californian seamounts	3	5,800	S	Goldberg and Arrhenius (1958)
North Pacific	2	2,450	S	Goldberg and Arrhenius (1958)
Area north of equator	4	6,100	W ?	Grim *et al.* (1949)
Trench NNW Sixty Mile Bank	2	2,700	W ?	Grim *et al.* (1949)
Indian Ocean	18	610	S	Katchenko and Flegontova (1964)
Area north of equator	8	2,120	S	El Wakeel and Riley (1961a)
Indian Ocean equator area	2	1,330	S	El Wakeel and Riley (1961a)
Area north of equator	20	8,050	S	Young (1954)
Area south of equator	1	300	X	Wedepohl (1960)
From all over the Pacific	9	6,700	X	Wedepohl (1960)
Average of Pacific clays	82	4,160		
		b) Deep sea carbonates[b]		
Atlantic and Mediterranean				
Caribbean Sea	2	210	S	Ericson and Wollin (1956)
Mid Atlantic Ridge	1 (9)	689	N/R	Turekian (1968)
Various places	4	190	S	Turekian and Wedepohl (1961)
North Atlantic (with clay)	4	840	S	El Wakeel and Riley (1961a)
South Atlantic off Africa	1	1,900	S	El Wakeel and Riley (1961a)
Mediterranean	2	1,600	S	El Wakeel and Riley (1961a)
Pacific and Indian Ocean				
Equatorial area, East Pacific (manganiferous)	2	5,000	S	Goldberg and Arrhenius (1958)

Table 56-K-1. (Continued)

Origin	No. of samples	Ba content ppm	Method	References
Equatorial area, Central Pacific	1	680	S	El Wakeel and Riley (1961a)
North equator area, Central Pacific	3	540	S	Young (1954)
		c) Deep sea siliceous muds		
Atlantic				
Atlantic off African coast	1	700	S	El Wakeel and Riley (1961a)
Equatorial area, Central Pacific	3	3,470	S	El Wakeel and Riley (1961a)
Central northern Pacific	6	10,400	S	Young (1954)
Central equatorial Pacific	3	8,100	S	Young (1954)

[a] Deep-sea clays calculated on $CaCO_3$ free basis.

[b] Raw analyses of carbonate rich cores but not necessarily indicative of the pure carbonate fraction.

closer to the continents are normally lower than the Central Ocean areas, but just off the coast of Africa (20 to 25° S), an area with values of $>4{,}000$ ppm Ba was detected.

Turekian (1968) has analyzed samples from different depths in a deep sea core for Ba. Concentrations range between 1,700 and 6,700 ppm Ba (calculated $CaCO_3$ and salt free); they indicate changes in the rate of Ba deposition within the last 30,000 years. Accumulation rates for Ba reported by Turekian (1968) vary from $<90\,\mu g/cm^2$ per 1,000 years to $790\,\mu g/cm^2$ per 1,000 years within the special core and are about $1{,}000\,\mu g/cm^2$ per 1,000 years in the Antarctic. In Table 56-K-1, averages for Ba are calculated using the "reduced $CaCO_3$ free" data. This means that the actual data may be lower.

Deep sea carbonates. Foraminifera ooze high in carbonate contains low Ba concentrations (10 to 30 ppm, Table 56-L-2). The barium content in carbonate sediments is either due to $BaSO_4$ or to manganese oxides or clay. Since all these sources may be active at the same time and do not work coherently, a recalculation to "pure carbonates" is very difficult. Turekian and Tausch (1964) extrapolated deep-sea cores in the North Atlantic to 100% $CaCO_3$ and got 10 to 30 ppm Ba for the pure carbonate. The available data are given in the table. The value of 190 ppm Ba by Turekian and Wedepohl (1961) for deep sea carbonates derived from 4 globigerina oozes from Atlantic cores is as yet the best information.

Manganese nodules cover wide areas of the deep sea bottom of all oceans and contain upto 20,000 ppm Ba. A survey by Puchelt (1967) of published literature shows that the Ba means are 4,500 ppm, 5,200 ppm and 3,700 ppm Ba for nodules from the Pacific, Atlantic, and Indian Oceans, respectively. In manganese nodules, Ba is either adsorbed, incorporated in acid soluble compounds (zeolites), or occurs as barite (Arrhenius, 1963).

Siliceous sediments occurring in deep areas of the oceans where carbonates are no longer stable can locally contain more than 1% Ba.

b) Shallow Water Sediments

The barium content of near shore and shelf sediments is influenced by the amount and kind of detrital matter and the barium content of the rivers. A review of literature by Puchelt (1967) shows that clay sediments of these areas are generally higher in Ba than sand and silt fractions. Clays from the Mississippi delta are especially high in Ba.

Three studies of reef carbonates (Stehli and Hower, 1961; Senakolis, 1964; Friedman, 1968) demonstrated that reef debris, reef material and oolitic muds contain only limited amounts of Ba. Stehli and Hower (1961) found a range from 10 to 61 ppm in 59 samples and an average of 18.4 ppm Ba. Friedman (1968) obtained spectrographically, 18 to 62 ppm Ba in corals with encrusting coralline algae, and 15.5 to 68 ppm Ba in carbonate sands from reef aprons. Carbonate sands with admixed terrigenous debris showed 130 to 280 ppm Ba. In the analysed samples, Ba concentrations change parallel to the "insoluble residue". Similar observations are reported by Senakolis (1964). Within the internal parts of the reef, average Ba content in clastic limestone was 3.1 ppm, peripheral parts of the reef had 436 ppm Ba.

II. Barium in Consolidated Sediments

a) Sandstones, Cherts, Graywackes

Pure quartz sandstones are very low in Ba, but since most sandstones contain considerable amounts of feldspars, these minerals are the most important Ba carriers besides micas, which occasionally occur. Pettijohn (1963) calculated the proportion of sandstone types to be 34% quartzite, 26% graywacke, 25% subgraywacke, and 15% arkose. This combination has an average K_2O content of 1.3%, to which a Ba content should be proportional. Comparison of the K/Ba ratios in low Ca granites and in sandstones and graywackes gives additional support to this proportionality. Single sandstones vary widely in Ba content, since even barite concentration (as cement) occurs locally (cf. Puchelt, 1967). If barite is a sandstone constituent, normally the weight ratio Ba/Sr is greater than 10, for barite generally contains much less than 10% $SrSO_4$. The Ba content of sandstones and graywackes ranges from 5 to 900 ppm. An average composition calculated from the European, Russian, and American sandstone and graywacke is 316 ppm Ba. This value is subject to changes when the individual data can be properly weighted. Nevertheless it is a more realistic value than the X0 ppm guess of Turekian and Wedepohl (1961). Cherts constitute a special group in silica sediments and always exhibit higher Ba means.

Table 56-K-2. *Barium in quartz sandstones, cherts, and graywackes*

Locality	No. of samples	Barium concentration range ppm	group mean ppm	total mean ppm	Method	References
Quartz sandstone						
Germany	73	50—810		406		
			134		X	Beetsch (1964)
			313		X	Wedepohl (1961)
			770		S	Zuelo (1963) see Puchelt (1967)
Sunda Islands	9	5—900	150		S	v. Tongeren (1938)
U.S.A.	289			280		Shoemaker *et al.* (1958)
			1,800		S	Young (1954)
U.S.S.R.	399	230—820		249		
			340		S	Babina and Kotorovich (1966) see Puchelt (1967)
			223		S	Lebedev (1967) see Puchelt (1967)
			140		S	Litvin (1961)
			250		S	Litvin (1963)
			290		S	Sinkarenko (1948)
Chert						
C.S.S.R.	2	300— 500		400	S	Leutwein (1957)
Finland	46	360— 630		495	S	Sahama (1945)
Germany	311	30—1,000		440	S S	Leutwein (1957) Prashnowsky (1957)
Indonesia	22	50—1,900		420		Audlee-Charles (1965)
Different places		350		350		Maxwell (1953) see Puchelt (1967)
Graywacke and arcose						
Africa				258	S	Danchin (1970) see Puchelt (1967)
Europe	51	189—670		370		
			290		S	v. Engelhardt (1936)
			360		S	Klein (1935)
			447		S	Kuenen (1941)
			389		S	Rivalenti and Sighinolfi (1969)
			270		X	Wedepohl (1961)
			335			Westermann (1961)
			500		S	Zurlo (1963) see Puchelt (1967)
North America	95	30—830		330		
					S	Macpherson (1958)
					S	Weber and Middleton (1961)
Indonesia New Zealand	12	30—480		252	S S	McLaughlin (1955) v. Tongeren (1938)

b) Shales

Ba averages for shales reported in the literature vary from 250 to 800 ppm (Puchelt, 1967; Vinogradov, 1956). The average of this paper is 546 ppm (s for the 25 means used: 212). Individual samples gave values from 10 to 5,000 ppm. From the data summarized in Table 56-K-3, it can be observed that especially low values have been found in shales of the Dnieper-Donets depression (Russia) and the west Siberian depression (Litvin, 1961, 1963; Tolkachev, 1968). If these low

Table 56-K-3. *Barium in shales*

Locality	No. of samples[a]	Barium concentration		Method	References
		range ppm	mean ppm		
Africa:	2	270—450	360		Junner and James (1947)
	25 (323)	394—1,004[b]	681	S	Danchin (1970)
Asia:					
Japan	1 (14)		540	X	Wedepohl (1960)
U.S.S.R.	8 (521)	150—370[b]	270	S	Babina and Kotorovich (1966)
	6 (920)	260—520[b]	394		Lebedev (1963)
	19	30—450	83		Litvin (1961)
	6 (32)	140—230	188		Litvin (1963)
	1		360		Sinkarenko (1948)
	5 (185)	140—220	182	S	Tolkachev (1968)
Europe:	1 (36)		800	X	Wedepohl (1960)
Finland	17 (105)	9—2,700	654	S	Sahama (1945)
Germany	3	480—540	513	S	Heide and Christ (1953)
	66	50—5,000	750	S	Leutwein (1951)
	3 (9)	700—900	824	S	Prashndwsky (1957)
	3	390—730[b]	527	S	Zurlo (1963)
Great Britain	24	210—2,240	739	S	Mohr (1959)
	6	330—1,050	555	S	Nicholls and Loring (1962)
	27	325—1,280	723	S	Spencer (1966)
Sweden			500	S	Landergren and Manheim (1963)
	9	450—2,150	866		Larsson (1932)
North America:	33	250—1,000	526	S	Degens *et al.* (1957)
	31	100—750	393	S	Fenner and Hagner (1967)
	41	10—1,020	470	S	Macpherson (1958)
	26	190—610	359	S	Murray (1954)
	15		580		Shaw (1954, 1957)
	17		720		Tourtelot (1957)
	3 (?)		750	S	Young (1954)
Pacific Islands:	2	500—1,050	775	S	El Wakeel and Riley (1961b)
	4	20—1,800	840	S	v. Tongeren (1938)

[a] No. of individual samples used for bulk samples, or for means, are given in parantheses.

[b] Range of means, not of individual samples.

values for Russia are omitted from averaging, the mean is 628 ppm with a standard deviation of 157 ppm.

Ba does not seem to be an environmental indicator for shales. Vine (1966) and Lebedev (1967) found a Ba increase in shales from fresh water to marine environment, while Murray (1954) reports opposite observations from Indiana and Illinois, USA. In general, shales have higher Ba contents than graywackes or sandstones, but locally, siltstones or sandstones may be higher in Ba (Alanov, 1963).

The mode of Ba binding in shales is complex. Several indications exist which point to a correlation of Ba with mica; parallelism with the amount of illite present has been found (Fenner and Hagner, 1967); and $BaSO_4$ was shown to be another possible carrier. Black shales often contain more Ba than normal shales thus suggesting a connection of Ba with organic matter. While certain shales retained their Ba content of deposition, others gained or lost some. Redistribution in diagenetic processes is possible.

c) Carbonate Rocks

Literature on Ba in carbonate rocks is summarized by Graf (1960) and Puchelt (1967). The Ba content of carbonate rocks varies from 1 to 10,000 ppm (cf. Puchelt, 1967). Using the literature cited in Table 56-K-4, an average Ba concentration for carbonate rocks of 90 ppm was calculated. This value is within the range reported by Graf (1960) (150 ± 110 ppm). Turekian and Wedepohl (1961) based their average limestone value (10 ppm) on the Ba content of modern molluscan shells. This value seems to be too low even for average carbonate, excluding detrital material. Means calculated by area as listed in Puchelt (1967) are plotted in Fig. 56-K-1.

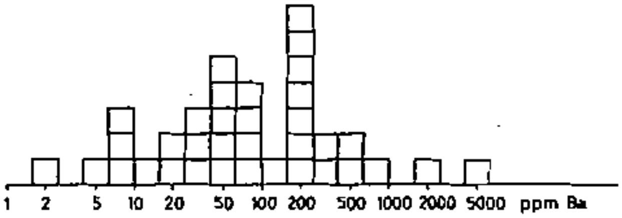

Fig. 56-K-1. Frequency distribution of Ba concentrations in carbonates (Puchelt, 1967)

High average Ba values in relation to the overall mean are reported for 10 Ordovician dolomites from Missouri, USA (620 ppm, Keller *et al.*, 1950), Cretaceous limestones, USA (900 and 1,800 ppm, Young, 1954), 91 Pennsylvanian limestones from Illinois, USA (260 ppm, Ostrom, 1957) and 6 limestones from Africa (1,330 ppm, Junner and James, 1947).

Ba in carbonate rocks originates mainly from 3 sources or processes:

1. detrital clay material,
2. redistribution during diagenetic processes, in which $BaSO_4$ can be precipitated,
3. incorporation of Ba in carbonate minerals.

In most cases processes 1 and 2 are quantitatively more important. Reference is made here to the difference between "pure" carbonates within recent reefs and carbonate sands from their peripheral parts (cf. chapter 56-K-I). In carbonate sands with detrital clay, Friedman (1968) observed an increase of Ba concentrations parallel to "insoluble residue". Fossil carbonate sediments exhibit similar features (Vinogradov *et al.*, 1952).

During evaporation of sea water, Ba is precipitated as barite which usually occurs disseminated in the calcium carbonate (Puchelt, 1967). Diagenetic alterations may cause local $BaSO_4$ concentrations. Thus Cameron (1966) found between 1 and 6,100 ppm Ba in a core from carbonate rocks within a distance of 80 feet. This diagenetic barite usually can be recognized under the microscope. Manganese-containing carbonate sediments are sometimes enriched in Ba (Mohr and Allen, 1965).

Table 56-K-4. *Barium in carbonate rocks*

Locality	No. of samples[a]	Barium concentration		Method	References
		range ppm	mean ppm		
Asia:					
Indonesia	4	9—450	220	S	v. Tongeren (1938)[b]
U.S.S.R.	8	30—240	65	S	Gorlitsky and Kaltaev (1962)
				S	Lebedev (1967)
					Litvin (1963)
	59 (2,973)	1—250	36	S	Ronov (1956)
	198	12—690	47		Sinkarenko (1948)
					Vinogradov and Ronov (1956)
Europe:					
Germany	41 (131)	1—300	62	S	v. Engelhardt (1936)
				S	Heide and Christ (1953)
				S	Prashnowsky (1957)
	125	15—403	92	X	Bajor (1965)
Great Britain	183	<5—8,000	220	S	Muir *et al.* (1956)
Roumania	15	10—300	100	S	Imreh and Ecaterine (1965)
Scandinavia	5	3—330	78	S	v. Engelhardt (1936)
				S	Henriques (1964)
				S	Sahama (1945)
North America:					
U.S.A.	10	200—2,000	620	S	Keller *et al.* (1950)[b]
	420	2—10,000	106		Cannon (1955)
				S	Lamar and Thompson (1956)
					Moore (1960)
				S	Ostrom (1957)
				S	Runnels and Schleicher (1956)

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[a] Number of individual samples used for bulk samples, or for means, are given in parantheses.

[b] Data not included in calculation of average.

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56-L. Biogeochemistry

Barium is present in recent and fossil plants, in animals and fuels. Ba accumulation in plants and animals was found by several investigators, but there is no evidence that this element is physiologically necessary. Ba is moderately toxic for plants and sligbtly toxic for mammals. Reviews of barium biogeochemistry are published by PUCHELT (1967) and BOWEN (1966), who also makes reference to earlier compilations.

BOWEN (1966) summarizes the available literature for Ba content in dry weights as follows:

marine plants	30 ppm
land plants	14 ppm
marine animals	0.2—3 ppm (higher in hard tissues)
land animals	0.75 ppm

I. Plants

In ash of marine plants, Ba varies over a wide range (Table 56-L-1). Coccoliths, which form the main constituents of marine carbonates, contain 10 to 30 ppm Ba in ash (TUREKIAN and TAUSCH, 1964). Ash of phytoplankton species from the Black Sea (*Chaetoceros Curvistus* and *Rhizosolenia Calcar Avis*) is very high in Ba (4,000 and 20,000—30,000 ppm, respectively; VINOGRADOVA and KOVAL'SKIY, 1962). Since these diatoms are very abundant in surface waters in summer, they form a considerable Ba enrichment, which may contribute to the Ba content of pelagic sediments. The tests of rhizosolenia and chaetoceros are very delicate and under marine conditions not stable. Thus they are subject to dissolution and are not to be found in sediments, although they certainly serve as barium conveyors to the sea floor (BRONGERSMA-SANDERS, 1967).

BOWEN (1966) reports concentration factors (ppm Ba in fresh organisms/ppm Ba in sea water) for plankton and brown algae to be 120 and 260, respectively.

Algae from the coast of Great Britain show seasonal variance in their Ba content in ash (upto 900 ppm Ba; BLACK and MITCHELL, 1952).

For terrestrial plants, an extensive study exists for bryophytes (SHACKLETTE, 1965). Some of the species investigated concentrate Ba considerably. The highest enrichment factor for Ba in bryophyte ash versus soil is 2,000. Equisetum (horsetail) ash was analysed by CANNON *et al.* (1968) and BOROVIK-ROMANOVA (1939). Ba content in ash of this plant (70 to 4,500 ppm) resembles approximately the concentration in the respective substrata.

Phanerogames reabsorb distinct amounts of Ba from the soil. Fir and spruce have 500 to 6,200 ppm Ba in ash with the highest concentrations in twigs (LOTSPEICH and MARKWARD, 1963). Black walnut, hickory, and red-ash leaves contain 870 to 2,570 ppm. Relative Ba enrichment was reported for oaks, which gave upto 2.30% Ba in the ash of twigs (BLOSS and STEINER, 1960). The average for Ba in ash of legumes is 1,420 ppm (CANNON, 1964).

Table 56-L-1. *Barium in plants*

Plant	Ba in dry tissue ppm	Ba in ash ppm	References
Schizophyta			
Bacteria	—62,000		Foerster and Foster (1966)
Phycophyta			
Coccoliths		10 — 30	Turekian and Tausch (1964)
Diatoms		20 —30,000	Vinogradova and Koval'skiy (1962)
Brown algae	0.4—120 ⌀ 31	270 — 900	Puchelt (1967)[a]
Red algae	50	0.6— 5.6	Puchelt (1967)[a]
Bryophyta	5—200 ⌀ 150	200 —50,000	Puchelt (1967)[a] Bowen (1966)[a]
Pteridophyta			
Equisitinae		30 — 4,500	Cannon *et al.* (1968)
Ferns	8		Bowen (1966)[a]
Spermatophyta			
Conifers		10 — 100 500 — 6,200	Puchelt (1967)[a] Lotspeich and Markward (1963)
Angiosperms	14		Bowen (1966)[a]
Deciduous trees		10 — 2,700 —23,000	Puchelt (1967)[a] Bloss and Steiner (1960) Robinson *et al.* (1950)
Legumes	average: 1,420		Cannon (1964)

[a] Compilations.

II. Animals

Organisms are only important for trace element geochemistry, if they occur in large amounts. Zooplankton (especially crustacees) from the Black Sea shows Ba accumulation upto 2,000 ppm in ash (Vinogradova and Koval'skiy, 1962). Since these animals constitute about 80% of the planktonic population in the survey area, they may also contribute to the Ba content of marine sediments.

Protozoan skeletons and shells consisting of $CaCO_3$ or SiO_2 contain upto 270 ppm Ba. They are the source for Ba in pelagic globigerina and radiolarian oozes. From investigations of Arrhenius (1963) it must be concluded that in Recent planktonic foraminifera, Ba is mostly bound to organic matter (upto 700 ppm in ash). In Table 56-L-2 the radiolaria Acantharia and the rhizopod Xenophyophora, which concentrate $BaSO_4$ in their skeletons, are listed. After death these skeletons are dissolved, but during this process they transport Ba towards the sediment. No fossil skeletons of these species are reported.

Goldberg and Arrhenius (1958) assume a certain Ba accumulation by digestion of benthonic organisms, since they found Ba enrichment in fecal pellets from the sea floor.

Table 56-L-2. *Barium in animals.* (Compilations by Bowen, 1966; Puchelt, 1967)

	Ba in dry tissue ppm	Ba in ash ppm	Ba in hard tissue ppm	Material in hard tissue
Protozoa[a]	10—270			$CaCO_3$
Foraminifera			180	$CaCO_3$
			500	SiO_2
Coelanterates	11—450		8.6—35[b]	$CaCO_3$
Corals				
Ctenophora		40—2,000		
Echinodermata	20— 50[c]		35	$CaCO_3$
Annelida (Vermes)		17— 50[d]		
Tentaculata				
Bryozoes		12—2,000[e]		
Brachiopodes				
Mollusca	3		<1—90[b]	$CaCO_3$
Lamellibranchiates	4— 75	4— 500	4—75[f]	
Gastropodes			4—50[g]	
Cephalopodes	7.2÷20			
Scaphopoda				
Arthopoda		15— 800		
Mammalia	2.3		6.9	apatite

[a] Radiolaria Acantharia contains 5,400 ppm Ba (Arrhenius, 1963), $BaSO_4$ is the hard tissue in the rhizopod Xenophyophora (Vinogradov, 1953).

[b] Including data by Friedman (1969).

[c] Upto 5,000 ppm Ba were found in dry tissue of *Asterias Linkii* from the Barents Sea.

[d] High values (1,000 to 1,500 ppm) are reported from Black Sea plankton (Vinogradova and Kovalskiy, 1962).

[e] Including data by Schopf and Manheim (1967).

[f] With certain species of Anodonta, Pecten, Astarte and Tellina, higher Ba concentrations (upto 500 ppm) were found.

[g] Some samples of Helix species, Littorina species, and Neptuna species contain upto 500 ppm Ba in their shells.

Much support for Ba in molluscan shells has been published (cf. Puchelt, 1967). Leutwein (1963) and Pilkey (1963) found a distinct Ba enrichment in Recent mollusc shells from fresh and brackish water environments. Obviously, the structure of the shells (calcite or aragonite) is of less importance as a cause of Ba incorporation than Ba content in the water and the environment. A reconstruction of palaeoenvironments from Ba concentrations of unaltered fossil shells has been attempted by Prokof'ev (1964), Friedman (1967) and others. Turekian and Armstrong (1960, 1961), investigating Recent and fossil shells, found Bato be much higher in molluscan shells of the Fox Hill Formation (Cretaceous), South Dakota, than in Recent species. According to their studies diagenetic alterations might considerably shift the initial trace element composition, even with only slightly altered mineralogy of the shell. Animals do not contain appreciable Ba concentrations. A few data from Bowen (1966) are included in Table 56-L-2. Additional references of detailed investigations are compiled by Gmelin (1960).

Table 56-L-3. *Barium in fuels*

Locality	Stratigraphy	Ba content in ash ppm	Method	References
Brown coal				
Australia	Permian-Tertiary	upto 800[a]	S	Swaine (1967) Brown and Swaine (1964)
Czechoslovakia	Tertiary	100— 1,000		Honek and Jirele (1965), see Puchelt (1967)
Germany	Tertiary	700— 7,600	X	Pietzner and Wolf (1964)
	Tertiary	200— 2,800	S	Rösler and Lange (1965), see Puchelt (1967)
U.S.A.	Tertiary	100—10,000	S	Breger *et al.* (1955), see Puchelt (1967)
			S	Brewer and Ryerson (1935), see Puchelt (1967)
	Cretaceous	100— 1,000	S	Deul and Annel (1956)
U.S.S.R.		140— 2,730		Tkachev *et al.* (1965)
Hard coal				
Australia	Permian	1,000—10,000	S	Clarke and Swaine (1962)
Canada		20— 2,200	S	Hawley (1955)
Finland		360— 1,600	S	Lokka (1943)
Germany	Carboniferous	100—27,000	S	v. Engelhardt (1936)
			S	Thilo (1934), see Puchelt (1967)
			S	Leutwein and Rösler (1956), see Puchelt (1967)
			S	Radmacher (1965), see Puchelt (1967)
	Permian	100— 500	S	Leutwein and Rösler (1956), see Puchelt (1967)
	Triassic, Jurassic	100	S	Leutwein and Rösler (1956), see Puchelt (1967)
Great Britain	Carboniferous	90— 710	S	Nicholls and Loring (1962), see Puchelt (1967)
			S	Gibson (1963)
New Zealand		250— 8,400	S	Brown and Taylor (1960) Coal Res. Company (1949)
Norway		average: 4,000	S	Butler (1953)
U.S.A.		270—22,000	S	Headlee and Hunter (1953), see Puchelt (1967)
Oils and bitumina				
Germany	Triassic—Cretaceous	—10,000	S	Heide (1938), see Puchely (1967)
U.S.A.	Cambrian—Tertiary	X—X 00,000	S	Bell (1960), see Puchelt (1967)
			S	Erigkson *et al.* (1954), see Puchelt (1967)
			S	Hyden (1961)
U.S.S.R.	Devonian—Tertiary	100— 3,000		Katchenkov (1951), see Puchely (1967)

[a] Ba concentration in dried coal.

III. Fuels (Including Coal)

Fuels of all geologic ages contain Ba in their ashes; often in amounts considerably above the earth's crust mean (Table 56-L-3).

From Ba data in Recent plants it can be deduced that at least part of the barium originates from living plants. During diagenetic alteration, humic acids may absorb additional Ba from the involved solutions. Extremely high Ba values of coal ashes (upto 4.76%), as reported from Great Britain (REYNOLDS, 1939), may be caused by a secondary $BaSO_4$ mineralization. No general trend of Ba concentration with maturity of coal could be observed. In one instance, LEUTWEIN (1966) paralleled Ba content with the amount of clays in a brown coal profile. ERSHOV (1958) carried out several electrodialysis experiments on coal samples and concluded that Ba—in addition to other elements—was present either as soluble minerals or in weakly absorbed form. It is not bound as strongly as Ge, which could not be extracted by this procedure.

It is to be assumed that Ba is incorporated in certain metallic-organic compounds in oil, but no investigations on the specific types have been published.

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56-M. Abundance in Common Metamorphic Rock Types

Barium concentrations in metamorphic rocks exhibit a large variation within each type (Table 56-M-1). They vary as widely as do values for all igneous and sedimentary rocks. Consequently, no meaningful Ba averages can be calculated. The only exception seems to be eclogites which form under special pressure conditions. Comparison of Ba concentrations in typical metamorphic minerals such as sillimanite, staurolite, garner etc., show that these structures have no appreciable tolerance for Ba.

Data on Ba distribution between coexisting minerals in metamorphic rocks are included in Table 56-D-5.

Table 56-M-1. *Barium in metamorphic rocks*

Rock type and locality	No. of samples	Barium concentration range ppm	mean ppm	Method	Reference
Gneiss, Randesund, Norway	8	<100— 1,060	<605	X	Ball (1966)
Slightly altered gneiss, Adirondacks, U.S.A.	10	220— 1,400	610	S	Engel and Engel (1958)
"Granitized" gneiss, Adirondacks, U.S.A.	18	125— 2,600	980	S	Engel and Engel (1958)
Gneiss, Montana, U.S.A.	7	1,800— 3,800	2,580	S	Foster (1962)
Gneiss, Langoy, Norway	5	823— 1,300	1,050	S	Heier (1960)
Gneiss, Lewisian, Inverness-shire, Scotland	4	300— 920	520	S	Lambert (1964)
Basic gneiss, Scotland	8	20— 300	110	S	O'Hara (1961)
Gneiss, S.W. Finland	40	<340— 654	≦430	S	Parras (1958)
Glaucophane schist, California, U.S.A.	11	7— 300	92	S	Coleman and Lee (1963)
Pelitic schist, Connemara, Eire	16	550— 1,850	1,300	S	Evans (1964)
Sillimanite schist, Montana, U.S.A.	2	1,300+ 1,900	1,600	S	Foster (1962)
Schist, Moine, Inverness-shire, Scotland	5	800— 1,440	970	S	Lambert (1964)
Phyllite, Finland	174	90— 1,500	552	S	Lonka (1967)
Quartz-albite-biotite schist, New Zealand	8	450— 1,500	690	S	Taylor (1955)
Greenschist, New Zealand	6	10— 125	34	S	Taylor (1955)

Table 56-M-1. (Continued)

Rock type and locality	No. of samples	Barium concentration		Method	Reference
		range ppm	mean ppm		
Hornfels, Connemara, Eire	11	670— 2,000	1,210	S	Evans (1964)
Hornfels, Palaman district, India	7		160	S	Ghose (1966)
Amphibolite, Randesund, Norway	17	260— 680	450	X	Ball (1966)
Amphibolite, Brazil	20	21— 270	67	S	Barros-Gomes *et al.* (1964)
Amphibolite, Adirondacks, U.S.A.	16	42— 140	84	S	Engel and Engel (1962)
Sericitite and biotite-amphibolite, Adirondacks, U.S.A	11	140— 1,650	220	S	Engel and Engel (1962)
Amphibolite, Australian shield	61	<610—> 990	817	X	Lambert and Heier (1968)
Amphibolite, S. W. Finland	20		251	S	Parras (1958)
Granulite, Australian shield	89	<420—>1,090	720	X	Lambert and Heier (1968)
Metabasite, Saxonia, Germany	9	100— 125	110	S	Mathé (1969)
Charnockite, Finland	29		570	S	Parras (1958)
Paracharnockite, Finland	24		672	S	Parras (1958)
Eclogite, Naustdal, Norway	1		<5	S	Binns (1967)
Eclogite, Nordfjord, W. Norway	6	<10— 30	≦20	S	Bryhni *et al.* (1969)
Eclogite, California, U.S.A.	2	15+ 300	160	S	Coleman and Lee (1963)
Eclogite, different places	5	5.6—136	56	I	Griffin and Murthy (1968)
Eclogitic rock, Münchberg, Germany	18	<100— 355	≦190	S	Hahn-Weinheimer (1959)

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56-N. Behavior in Metamorphic Reactions

Only very few investigations exist on Ba behavior under metamorphism. LONKA (1967), analyzing Precambrian phyllites of Finland, observed no differences in Ba concentration between phyllites of lower and higher degree of metamorphism. Trace element data including Ba concentrations have been used by TAYLOR (1955) to discuss the origin of New Zealand metamorphic rocks under the assumption of isochemical metamorphism.

In the Adirondacks, New York, ENGEL and ENGEL (1958) studied progressive metamorphism and granitization of the major paragneiss. They found Ba to decrease with increasing metamorphism, while the Ba content in biotites increased (580, 717, 888, 1,766 ppm). Granitized gneisses of this area generally showed much higher Ba values than normal gneisses. TUREKIAN and PHINNEY (1962) could not detect characteristic changes of Ba content in garnets and coexisting biotites in a metamorphic sequence from Nova Scotia.

A special feature of transport during metamorphism is skarn formation. HIGAZY (1952) observed an increase of Ba content from epidiorite, 90 ppm (S), to biotite-epidiorite, 270 ppm, to biotite skarn, 910 ppm. The subsequent alteration to lepidomelan-skarn (720 ppm) and chlorite-skarn (270 ppm) caused distinct decreases in Ba. NESTERENKO *et al.* (1958) found Ba to be depleted from biotite hornfels when this rock was altered to pyroxene-garnet-skarn.

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56-O. Relations to Other Elements, Crustal Distribution, Economic Importance etc.

I. Inter-element Relationships

In igneous rocks, Ba generally substitutes for K in silicate structures. A certain correlation of Ba and Ca in igneous rocks with low K was demonstrated in sections 56-D and E. In the sedimentary cycle, Ba preferentially occurs as barite, in clays and in feldspar. Presence of barite is dependant on sulfate abundance, which in turn requires suitable redox conditions. In sediments, including evaporites, the correlation Ba-K is much less pronounced than in igneous rocks. The substitution Ba-Ca observed in few carbonate minerals is of less general importance.

II. Distribution in the Earth's Crust

Details discussed in the preceding sections are summarized in the following table:

Table 56-O-1. *Abundance of Ba in important masses of the earth's crust. (Means calculated on the basis of* WEDEPOHL'S, 1969, *data on the abundance of rock units)*

Igneous intrusive rocks (mean)	728 ppm
Gabbroic rocks	246 ppm
Granites	732 ppm
Granodiorites and quartzdiorites	873 ppm
Diorites	714 ppm
Consolidated sediments (mean)	538 ppm
Sandstones (including graywackes)	316 ppm
Shales	628 ppm[a]
Carbonate rocks	90 ppm
Sea water	0.020 ppm

[a] 546 ppm, if the Russian shales low in Ba are included.

A discrepancy exists between the Ba means for consolidated sediments and magmatic rocks. Part of the Ba missing in the fossil sediments is bound in pelagic clays (mean Ba content 2,000 to 3,000 ppm; cf. Table 56-K-1) which constitute at least 10% of the total sediment mass (WEDEPOHL, 1969). But part of the discrepancy may be due to the fact that the individual data used for the averages could not be weighted properly for the compilation.

III. Technical and Economic Importance

Barite and witherite are the only barium minerals of economic interest. Descriptions of deposits and their production are given by GMELIN (1960), BROBST (1970) and others. World production of barite has been almost constant since 1964 at about 4 million short tons per year (ORR, 1970; for detailed information see U.S. Geol. Surv. Bulletin 1321).

Barite is used for drilling muds in oil and gas geology (consuming about 75% of the world's production) and for radiation-shielding concrete. Chemically treated $BaSO_4$ of fine particle size is an important filling material in the rubber, paper, and fabric industries. It is one of the components of the white pigment "lithopone". Ba compounds are used in glass and enamel production as flows and for glasses with special optical properties. Barium chloride serves as a rat poison and insecticide; barium chlorate causes the green colour of pyrotechnics; barium titanate is a ferroelectric substance used in the electro-industry; certain barium compounds are the active substances of fluorescent screens.

Reviews on barium compounds and their industrial uses are given by STÖHR and FLASCH (1953), in GMELIN (1960), in RÖMPP (1966) and in KIRK and OTHMER (1958). A bibliograpby on barium chemistry was compiled by SCHWIND (1952).

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