# Reports

## Origin of High-Alumina Basalt, Andesite, and Dacite Magmas

Abstract. *The typical volcanic rocks of most island arcs and eugeosynclines, and of some continental environments, are basalt, andesite, and dacite, of high alumina content. The high-alumina basalt differs from tholeiitic basalt primarily in having a greater content of the components of calcic plagioclase. Laboratory data indicate that in the upper mantle, below the level at which the basaltic component of mantle rock is transformed by pressure to eclogite or pyroxenite, the entire basaltic portion probably is melted within a narrow temperature range, but that above the level of that transformation plagioclase is melted selectively before pyroxene over a wide temperature range. The broad spectrum of high-alumina magmas may represent widely varying degrees of partial melting above the transformation level, whereas narrow-spectrum tholeiite magma may represent more complete melting beneath it.*

The characteristic rocks of most of the volcanic island arcs about the northern and western Pacific Ocean are high-alumina basalt, andesite, and dacite (*1*). Andesite is the most abundant, but any of the three main types may dominate within one temporal or spatial part of a province. Rhyodacite and quartz latite are generally much subordinate. Different types may erupt simultaneously from adjacent volcanoes or consecutively from one vent. Rocks of each arc have a broad frequency distribution (*2*; *3*, Fig. 65) with regard to silica and other components, rather than a narrow one as have rocks of most tholeiitic and olivine-basaltic provinces, and they have a markedly higher bulk-average silica content than basaltic assemblages do. High-alumina rocks generally contain abundant phenocrysts of plagioclase. Orthorhombic and monoclinic pyroxenes occur together in most of the andesites and in some of the basalts and dacites.

The volcanic rocks of many ancient eugeosynclines, now parts of the continents, are high-alumina rocks petrologically so similar (*3*, p. 71; *4*) to the rocks in the island arcs that they presumably formed in similar environments. Such continental volcanic chains as the Cascade Range of the western United States (*5*) and the Andes of South America are characterized by similar high-alumina rocks. Tholeiitic basalt is related in origin, for it is associated intimately with high-alumina rocks in some provinces and is the sole or dominant volcanic type in some island-arc and eugeosynclinal assemblages. Spilitization—the removal of primary calcium and addition of secondary sodium—has affected many of the eugeosynclinal and older island-arc rocks, but since the process is nonmagmatic (*6*) it need not be considered with the problem of the origin of high-alumina magmas.

The contrast between tholeiite and the high-alumina association is indicated by Table 1. High-alumina basalt is markedly lower in magnesium, iron, and titanium than average tholeiite, and it is markedly higher in sodium and, of course, aluminum. Bulk composition of the high-alumina association is approximated by the composition of the andesite and differs from tholeiite in the same respects and also in being less calcic and more silicic.

Explanations advanced for the origin of high-alumina magmas include crystal-settling differentiation of basaltic magma (*7*), incongruent melting of enstatite in mantle periodotite (*8*), assimilation of continental crust (*2, 4*) or of aluminous (*9*) or other (*5*) sedimentary rocks in basaltic magma, direct melting of continental crust (*4*), and melting of crustal rocks carried deep beneath the arcs by faults (*10*) or downbuckles (*5, 11*).

Serious objections apply to all of these hypotheses. Osborn's differentiation scheme (*7*, Figs. 13 and 14) requires that all crystallization occur under severely limited conditions (*12*), and that always at least one-third, on average two-thirds, and on frequent occasion perhaps 95 percent, of the initial magma be precipitated before eruption, despite the uniformity of variation pattern of the erupted lavas and the general scarcity of mafic phenocrysts. The enstatite-melting hypothesis is based on calculations of bulk chemistry involving an assumed mantle composition and the composition of the basalt alone of the high-alumina suite. No consideration is given by this hypothesis to the bulk of the suite, which is more silicic than basalt, and the hypothesis is unsupported by high-pressure laboratory data (*12*, p. 411), seismic velocities (*13*), or the character of mantle xenoliths in kimberlite (*14*). Island arcs are developed typically across oceanic crust (*15*) so that continental crust cannot be invoked to explain high-alumina magma, and higher contents of potassium would be expected if continental rocks were involved. Aluminous sedimentary rocks are so nearly lacking in most eugeosynclines that they generally cannot be incorporated. Although deep earthquake foci lie behind island arcs and shallow ones are concentrated in front of them, the distribution is much too irregular to be interpreted as representing simple faults (*16*), and indeed there is no requirement that the deep earthquakes represent fault motions at all (*17*). Hypotheses concerning downbuckling remain extremely speculative.

Yoder and Tilley (*12*, pp. 421–422) inferred that high-alumina magmas form by partial fusion, or as residual liquids, under conditions of high water pressure. A similar rationale forms part of the suggestions made here.

Limited seismic evidence suggests that magma is generated at a depth of about 60 km beneath the Kurile Islands (*18*). In this chain, velocity inversion occurs in the uppermost mantle, seismic velocity decreasing downward (*19*). The inversion may be due to a worldwide low-velocity layer within which most magmas are generated, and within which the crust and uppermost mantle are uncoupled from the rest of the mantle (*20*).

No differentiation scheme yet suggested appears to account satisfactorily for either the characteristics of or the variations within the high-alumina as-

Table 1. Chemical composition, in percentage by weight, of tholeiite and of representative rock types of the high-alumina association.

| Oxide | Tholeiite (av) (*23*) | High-alumina association* | | |
|---|---|---|---|---|
| | | Basalt | Andesite | Dacite |
| $SiO_2$ | 50.8 | 51 | 56 | 61 |
| $Al_2O_3$ | 14.1 | 18 | 17 | 16.5 |
| Iron† | 11.7 | 9 | 8 | 6 |
| MgO | 6.3 | 5 | 3.5 | 2.5 |
| CaO | 10.4 | 11 | 8 | 6 |
| $Na_2O$ | 2.2 | 3 | 3.5 | 4 |
| $K_2O$ | 0.8 | 0.7 | 1 | 1.5 |
| $TiO_2$ | 2.0 | 1 | 1 | <1 |

* Scaled, at $SiO_2$ values specified, from Hamilton (*3*, Fig. 65). † As FeO.

sociation, and (in contrast with differentiated-basalt assemblages) there is no frequency-distribution peak composition to suggest the existence of any single parental magma type. The lack of any marked peak composition also is evidence against formation of the variants by assimilation of any material in any primary magma type. The likely explanation of the broadness of the compositional spectrum is in variable degrees of partial melting of mantle material. If this is correct, then the limitation is imposed on that mantle material that it must melt over a broad temperature range rather than within a narrow one. Relatively uniform basaltic magma series, by contrast, must originate under conditions in which the basaltic component of the mantle melts within a narrow temperature range.

Heat-flow and laboratory data indicate that most basaltic magma is generated high in the mantle but beneath the pressure-transformation level where the light plagioclase and low-pressure pyroxene of gabbro are converted to the dense alkali-bearing aluminous pyroxenes and iron-magnesium garnet of pyroxenite and eclogite (*21*). These dense minerals melt together in the laboratory over a relatively narrow temperature range under both anhydrous (*12*, Tables 43–45) and hydrous (*12*, Tables 46 and 47) conditions at pressures appropriate to the upper mantle. Tholeiite and olivine-tholeiite magma probably originate by the nearly complete fusion, within such a narrow temperature range, of the pyroxenitic or eclogitic fraction of mantle rock, leaving residual unmelted olivine. [Yoder and Tilley (*12*, pp. 509, 520) suggested that partial melting of the basaltic component of eclogite produces tholeiite magma at relatively low pressure and alkaline basalt magma at high pressure. Their mechanism—shifts with pressure in the melting relations of garnet and pyroxene—would, however, result in changes in silica content opposite to those required and hence cannot operate.] At lesser pressures in the upper mantle, aluminous orthopyroxene might be left in the unfused residuum, or else might be precipitated by partial crystallization of olivine tholeiite generated deeper (*22*); in either case a magma of moderately alkaline olivine-basalt composition would be left.

Table 2. Calculated combinations of average tholeiite and ideal-composition plagioclase, in percentage by weight.

| Oxide | 75% tholeiite plus 25% $An_{65}$ | 65% tholeiite plus 35% $An_{25}$ |
|---|---|---|
| $SiO_2$ | 51 | 55 |
| $Al_2O_3$ | 18.1 | 17.4 |
| Iron* | 8.8 | 7.6 |
| MgO | 4.7 | 4.1 |
| CaO | 11.0 | 8.3 |
| $Na_2O$ | 2.7 | 4.4 |
| $K_2O$ | 0.6 | 0.5 |
| $TiO_2$ | 1.5 | 1.3 |

* As FeO.

The curves of actual temperature and of the melting temperature of the basaltic component of the mantle must be close together and subparallel within a considerable thickness of the upper mantle (*21*). Presumably the curves cross only within those parts of the Gutenberg low-velocity zone which underlie active volcanic provinces. At a depth varying from perhaps 40 km under conditions of low heat flow to 60 km with high heat flow (*12*, Fig. 43) the basaltic component of the mantle probably is converted to either broad-composition pyroxenite or to eclogite. Where upper-mantle temperature is high, so that the transformation is depressed toward its deeper limit, the melting temperature of the fraction with the composition of basalt may be reached above the zone of pressure transformation. The minerals which would melt under these conditions should be plagioclase and amphibole or low-alumina pyroxene.

At low pressure and under hydrous conditions, plagioclase begins to crystallize, or completes melting, at a temperature higher than does pyroxene (*12*, Figs. 27–30); under anhydrous conditions, either pyroxene or plagioclase may be the higher-temperature phase, but there is little difference in temperature between their appearances (*12*, Fig. 6). In both instances, plagioclase and pyroxene melt or crystallize together over most of their range. The crystallization and melting relations are quite different at pressures appropriate to the upper mantle, at least under hydrous conditions, for plagioclase then is a markedly lower temperature mineral than is either pyroxene or amphibole, and the temperature range of crystallization or melting is broad. Partial fusion of the basaltic component of mantle rock, which probably has a bulk composition near that of basalt plus much forsterite, would necessarily under such conditions yield magma relatively richer in plagioclase than would the fusion of all of the basaltic component. Sodic plagioclase melts before calcic, and if the basaltic component does not melt completely the resulting magma will be more sodic and silicic. Magmas of the high-alumina association may therefore be generated by partial melting of the basaltic component of mantle rock above the level of transformation of that component to pyroxenite or eclogite.

The composition of high-alumina basalt closely matches that of combined average tholeiite and calcic plagioclase, and the composition of andesite matches less well that of tholeiite plus more sodic plagioclase. This is illustrated by calculated combinations of tholeiite (as in Table 1) plus ideal-composition plagioclase (Table 2). The composition of dacite, however, cannot be approximated by any combination of only plagioclase and tholeiite.

The more complete the melting (as shown by the increasingly calcic composition of the melt) of the plagioclase, the greater should be the melting of the rest of the basaltic (tholeiitic) component of the mantle rock. The less complete the melting, the more selective will it be of the silicic components of the rock. The spectrum of composition within high-alumina rocks reflects varying degrees of partial melting.

A corollary of this hypothesis is that any intermediate or silicic plutonic or volcanic rock (quartz diorite to granite, dacite to rhyolite) that represents a directly mobilized magma (rather than a differentiate) was generated above the level of transformation of gabbro to eclogite, whether within the crust or mantle.

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3 September 1964

## Sea Water: Saturation with Apatites and Carbonates

Abstract. *Pacific Ocean water, on the average, appears to be slightly supersaturated at all temperatures with hydroxyapatite and carbonate fluorapatite. Water above 14°C is saturated with calcite, whereas water above 20°C is saturated with aragonite.*

Approximately 1200 analyses of Pacific Ocean water were examined to determine the average degree of saturation of sea water with hydroxyapatite, carbonate fluorapatite, calcite, and aragonite as a function of temperature (*1*). Calculations involving a large number of data in depth (approximately 0 to 3000 m) and area should show the general saturation level of the oceans with respect to the four minerals and should show temperature-saturation trends if present. The trends can be used to construct dynamic models for determining environments of formation for the minerals. Only analyses listing temperature, $p$H, alkalinity, total phosphorus, and salinity were used. All calculations and plotting were done by computer.

The degree of saturation of sea water with respect to hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, may be determined by comparing $pK'_{ap}$ with $pK_{ap}$ (*2*):

$$pK'_{ap} = 10\,p(Ca^{2+}) + 6\,p(PO_4^{3-}) + 2\,p(OH^-) \qquad (1)$$

$pK_{ap}$ is 111.69 (0°C), 112.00 (5°C), 113.19 (15°C), 113.99 (25°C), and 114.40 (30°C) (*3*).

The degree of saturation of sea water with respect to a carbonate fluorapatite,

$$Na_{0.29}Ca_{9.56}(PO_4)_{5.37}(SO_4)_{0.30}(CO_3)_{0.33}F_{2.04},$$

may be determined by comparing $pK'_{cfap}$ with $pK_{cfap}$:

$$pK'_{cfap} = 0.29\,p(Na^+) + 9.56\,p(Ca^{2+}) + 5.37\,p(PO_4^{3-}) + 0.30\,p(SO_4^{2-}) + 0.33\,p(CO_3^{2-}) + 2.04\,p(F^-) \qquad (2)$$

$pK_{cfap}$ is 103 at 5°C and 105 at 25°C as determined in this laboratory for this carbonate fluorapatite.

The saturation of sea water with aragonite and calcite may be determined by comparing $pK'_{arag}$ with $pK_{arag}$ and $pK'_{calc}$ and $pK_{calc}$:

$$pK'_{arag} = p(Ca^{2+}) + p(CO_3^{2-}) \qquad (3)$$

$$pK'_{calc} = p(Ca^{2+}) + p(CO_3^{2-}) \qquad (4)$$

Activities of $Ca^{2+}$, $CO_3^{2-}$, $PO_4^{3-}$, $Na^+$, $SO_4^{2-}$, $F^-$, and $OH^-$ for substitution in Eqs. 1 through 4 are determined from the following relationships (*4*):

$$[\Sigma Ca^{2+}] = [Ca^{2+}] + [CaSO_4^0]$$

$$\text{Alkalinity} = 2[CO_3^{2-}] + 2[CaCO_3^0] + 2[MgCO_3^0] + 2[NaCO_3^-] + [HCO_3^-] + [CaHCO_3^+] + [MgHCO_3^+] + [NaHCO_3^0]$$

$$[\Sigma PO_4^{3-}] = [HPO_4^{2-}] + [H_2PO_4^-] + [NaHPO_4^-] + [KHPO_4^-] + [MgHPO_4^0] + [CaHPO_4^0] + [Ca_2 \cdot HPO_4 \cdot CO_3^0] + [Ca_2 \cdot PO_4 \cdot CO_3^-]$$

$$[\Sigma Na^+] = [Na^+] + [NaSO_4^-]$$

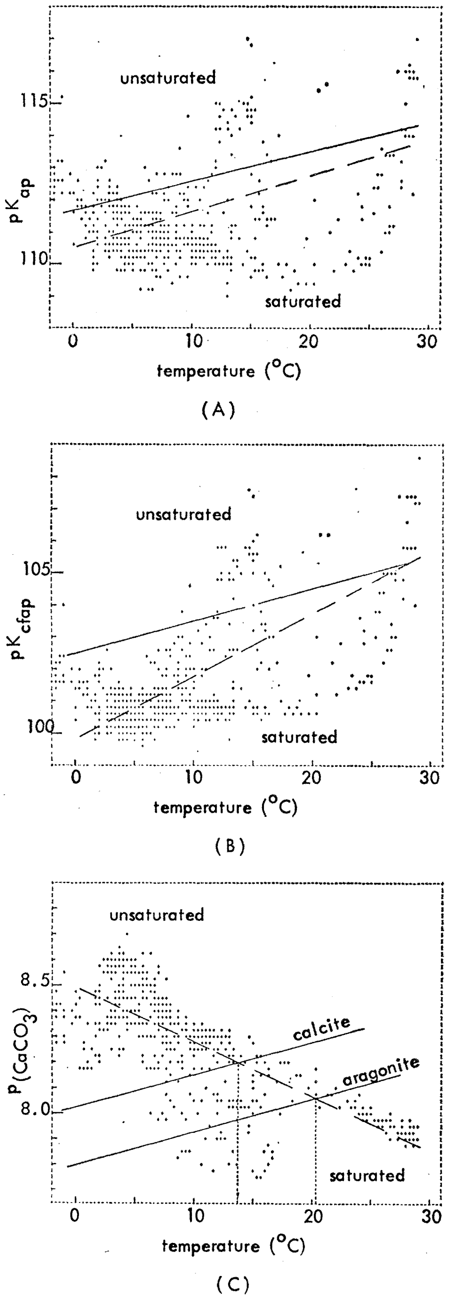
$$[\Sigma K^+] = [K^+] + [KSO_4^-]$$

$$[\Sigma SO_4^{2-}] = [SO_4^{2-}] + [MgSO_4^0] + [CaSO_4^0] + [NaSO_4^-] + [KSO_4^-]$$

$$[\Sigma F^-] = [F^-] + [MgF^+]$$

The values of $pK'$ in Eqs. 1 through 4 were plotted by computer, and a least-squares curve of the form, $pK' = (a/t) + b$, was fitted to the data. The dashed line in Fig. 1 is the least-squares fit to data, whereas the solid line represents the solubility constant as a function of temperature.

Sea water on the average appears to be supersaturated with respect to hydroxyapatite and carbonate fluorapatite as is shown by comparing dashed and solid lines in Fig. 1, *A* and *B*. There is, however, only a 1 to 2 percent difference from equilibrium values for the values of $pK'$. Arrhenius (*5*) found, contrary to these conclusions, that apatite is being dissolved in deep ocean water environments. Some of



(A)

(B)

(C)

Fig. 1. Saturation of sea water with hydroxyapatite (*A*), carbonate fluorapatite (*B*), and calcite and aragonite (*C*) as a function of temperature in the Pacific Ocean. Distribution of points represents spread of data and not total intensity. Dashed lines representing least-squares fit to ocean data have multiple correlation coefficients of 0.57, 0.77, and 0.85 for 1179 observations and for hydroxyapatite, carbonate fluorapatite, and calcium carbonate, respectively.