

or iron-rich granophyre, rather than an orogenic andesite, dacite or rhyolite. The fractionation trends as depicted on an FMA plot for the crystallization of a typical tholeiitic basalt and for the calc-alkaline series are quite different, indicating different mechanisms of origin. POLDERVAART and ELSTON (1954) list several specific limitations to BOWEN's hypothesis.

OSBORN (1959, 1962), on the basis of experimental studies on simple iron-bearing silicate systems under controlled oxidation conditions, suggested that the calc-alkaline rock suite may be derived by fractional crystallization of a basaltic magma under constant oxygen pressures, possibly achieved by high water vapour pressures. He claimed that under such conditions magnetite crystallised out early, relative to plagioclase. This prevented iron-enrichment and promoted silica-enrichment. However this mechanism does not generally satisfy the chemical and petrographic features of the rocks of the calc-alkaline series. For example, calc-alkaline rocks are not invariably significantly oxidized (Table 1), and many of the cases of marked oxidation may be attributed to late stage processes, such as sub-aerial oxidation during eruption. Also there is a general lack of evidence

Table 1. *Oxidation state of calc-alkaline rocks*

*Note:* Only a few selected analyses of calc-alkaline rocks are given; this is not intended as an exhaustive survey. The original oxidation state of the magma is likely to be lower than the figures listed because of the effects of high-level or sub-aerial oxidation of the analysed rocks.

Rock type	FeO	Fe <sub>2</sub> O <sub>3</sub>	FeO/Fe <sub>2</sub> O <sub>3</sub>	Reference
Basalt	6.69	1.51	4.4	WILLIAMS (1942)
	8.59	2.21	3.9	WILLIAMS (1933)
	6.41	1.24	5.2	WILLIAMS (1950)
Basaltic andesite	4.98	1.47	3.4	WILLIAMS (1942)
	5.07	1.91	2.7	WILLIAMS (1950)
	7.8	1.7	4.6	BYERS (1961)
Andesite	4.21	1.59	2.6	WILLIAMS (1942)
	4.00	0.97	4.1	WILLIAMS (1950)
	7.38	1.01	7.3	WILLIAMS (1935)
	5.93	2.23	2.7	SCHMIDT (1957)
	4.66	1.10	4.2	WILCOX (1954)
Dacite	2.56	0.37	6.9	WILLIAMS (1942)
	1.12	0.29	3.9	SCHMIDT (1957)
	3.61	1.12	3.2	COOMBS (1939)
Rhyolite	1.76	0.24	7.3	WILLIAMS (1935)
	1.53	0.88	1.7	WILLIAMS (1932)

for early crystallization of magnetite; instead there is abundant evidence for early crystallization of plagioclase, which greatly reduces the efficiency of OSBORN's model, particularly in the basalt to andesite part of the calc-alkaline series. The intermediate-acid members of the calc-alkaline series do not show marked depletion in Ti or V as would be expected (WAGER and MITCHELL, 1951) if an opaque mineral (e.g. titanomagnetite) was a key phase in the formation of such compositions (TAYLOR and WHITE, 1966; COATS, 1952, 1959; SNYDER, 1959; BYERS, 1961; DREWES *et al.*, 1961). There is little or no field evidence for an association of

opaque mineral-rich mafic crystalline residua with the development of the calc-alkaline series. Some of the Alaskan zoned ultramafic complexes have the appropriate composition, but it has been argued that these complexes formed from ultramafic magmas and in most cases show no evidence for residual crystal accumulation from a basaltic parent (RUCKMICK and NOBLE, 1959; TAYLOR and NOBLE, 1960; exceptions are described by IRVINE, 1963).

Recent work by CARMICHAEL (1967) on iron-titanium oxides occurring in some acid calc-alkaline rocks indicates that oxygen fugacity has not remained constant during fractionation in the volcanic series, as required by OSBORN's model. Also WILKINSON (1966) pointed out that titanomagnetites described from Japanese andesites (AKIMOTO, 1954, 1955) implied crystallization under conditions of low oxygen pressure. In other areas hornblendes and biotites in more acid members of the series show considerable iron-enrichment, not expected according to OSBORN's hypothesis (LARSEN and DRAISIN, 1950).

*b) Melting of Pre-Existing Sial, Hybridism or Mixing of Magmas*

Partial or complete melting of deep crustal sialic material of appropriate composition has been considered as a possible origin for the various members of the calc-alkaline series (HOLMES, 1932; HESS, 1960; TURNER and VERHOOGEN, 1960). When partial melting takes place magmas of rhyolitic composition may be produced first, followed progressively by dacite, andesite and finally basaltic andesite as the temperature of the partial melting increases.

Alternatively hybridization of the early formed acid magma may occur, producing more basic members of the calc-alkaline suite. Thus NOCKOLDS (1934) proposed that diorite, tonalite and granodiorite plutonic members of the calc-alkalite suite were derived from the interaction of acid quartzo-feldspathic magma with solid basic igneous material. WILKINSON (1966) elaborated on this mechanism, proposing hybridization of an acid magma by dioritic rocks, and WILKINSON *et al.* (1964) described an adamellite-porphyrite from New England which demonstrated hybridization of a low melting silicic alkalic liquid by a biotite diorite.

Mixing of acid and basic magmas has been suggested as a means of deriving magmas of intermediate composition. The basic magma is derived from the mantle while the acid magma comes from melting of sialic crustal material. Mixing of magmas has been demonstrated in some instances (LARSEN *et al.*, 1936; WILLIAMS *et al.*, 1955; MACDONALD and KATSURA, 1965).

All these theories involving development of magma from sialic material fail to explain the origin of calc-alkaline rocks occurring along the borders of some ocean basin regions where there is no sialic material available e.g. calc-alkaline rocks in island arc regions developed across oceanic crust as in the Kuriles (KOSMINSKAYA, 1963), Aleutians (SHOR, 1964) and the Marianas Islands (GORSHKOV, 1962). Similarly these theories cannot account for the evolution of sialic continents from the earth's mantle as implied in the hypotheses of RUBEY (1955), WILSON (1954) and ENGEL (1963). In addition some geochemical data on the calc-alkaline suite precludes large scale involvement of sialic material in its genesis. Thus low initial strontium isotope ratios found for calc-alkaline rocks from many localities (TAYLOR and WHITE, 1965; HURLEY *et al.*, 1965 and EWART and STIPP, 1967) indicate that