SKELETAL CRYSTALLIZATION OF PSEUDOBROOKITE

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Abstract

An unusual occurrence of skeletal pseudobrookite and equant ulvospinel is shown, by microprobe analysis, to represent disequilibrium crystallization in a rapidly quenched dike cutting the White Mountain batholith of New Hampshire. It is suggested the skeletal microtextures are themselves indicators of chemical disequilibrium in magmatic systems.

INTRODUCTION

The growth of skeletal crystals results from various physical-chemical conditions: undercooling or super-saturation of melts, slow diffusion rates and a critical amount of impurity in the solvent phase, and temperature gradients and vectorial thermal conductivities in the growing crystal. The phenomenon is so common in metallurgy that it is surprising to find relatively few references to skeletal crystal in the geological literature. Rosenbusch (1924, Plate IX) figures skeletal magnetite and augite in glassy lavas, and Shand (1947, p. 108) cites occurrences of skeletal apatite and sphene; yet standard reference works are notably silent concerning dendritic and skeletal microtexture.¹ It is with this fact in mind that we offer the following observations concerning unusually well-developed skeletal pseudobrookite in several of the lamprophyres and related dikes which cut Early Jurassic plutons and older metamorphic formations of central New Hampshire.

FIELD RELATIONS AND PETROGRAPHY

The dike chosen for detailed analysis cuts the Conway granite of the White Mountain batholith 7.2 miles east of Lincoln, N. H., on the Kancamagus Highway (44°02′26″N, 71°32′40″W). The dike is 12 to 16 inches wide and shows a well-developed cryptocrystalline chill zone at the contacts grading into a fine-grained aphanitic texture at the center. Although related to camptonite dikes found elsewhere in the Franconia quadrangle and also in the Holderness quadrangle further south, this

¹ The terms "dendrite" and "skeletal crystal" are hopelessly scrambled in the mineralogical-petrological literature. We adopt the term "skeletal crystal" for the forms pictured here (Figs. 1 and 2) because they do not show the branching or arborescent shapes characteristic of typical dendrites.

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dike lacks the characteristic barkevikite and/or augite phenocrysts of camptonites, and is thus somewhat atypical of the other lamprophyres. Two generations of plagioclase make up approximately 60 percent of the modal volume. Phenocrystal plagioclase is andesine $(An_{40}-An_{50})$ which is generally homogeneous and shows evidence of sericitic alteration. The more abundant groundmass plagioclase is labradorite $(An_{48}-An_{67})$ which occurs as small, moderately zoned laths. Opaque minerals (15%) include pyrite, polyhedral ulvospinel, and skeletal pseudobrookite. The habit of the pseudobrookite (Figures 1 and 2) is spectacular: throughout the rock are extensive, 3-dimensional, rectilinear lattices composed of branching arms <6 μ m thick and up to 250 μ m long. The lattices are typically



FIG. 1. Skeletal pseudobrookite, ulvospinel (irregular opaque grains), and pyrite (opaque cubes) in plexus of plagioclase, sphene, calcite, and chlorite. Bar scale equals 0.1 mm.



FIG. 2. Growth points on skeletons. Note the rectilinear axial directions. Bar scale equals 0.025 mm.

confined to and transgress areas of plagioclase; but occasionally they abut larger plagioclase laths, suggesting nearly simultaneous crystallization. Extensive alteration of the dike has yielded calcite (10%) and chlorite (5%), both of which appear to be partly pseudomorphous after pyroxene. Biotite is scarce (5%) and is only found as small (<0.5 mm) blades in the groundmass. Also present in trace amounts are apatite (partly skeletal), sphene, metamict zircon, rutile (?), hematite (?), and an unidentified zeolite.

The peculiarly jumbled pattern of the pseudobrookite skeletons (Figure 1) suggests that very rapid crystallization produced the latticeworks of this oxide just prior to solidification of the dike, and that for a brief time the latticeworks were suspended in a viscous, moving silicate melt. The general shape of the pseudobrookite latticeworks is that of flattened parallelpipeds, which suggests that the arms may correspond to the a, b, and c crystallographic directions. Because of their very small size, however, we have not been able to make positive morphological identifications, nor can we dismiss the possibility of twinning—as in the very similar rutile latticeworks.

MINERAL CHEMISTRY

Compositions of minerals in the dike are given in Table 1. These analyses were performed on a MAC model 400 electron microprobe (20 kV, 0.01 μ A) using a variety of natural and artificial mineral standards. The data were reduced by an iterative program (Probeg IV) which applied beam current drift, background, absorption, fluorescence, atomic number, and dead time corrections.

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	Plagioclase	Calcite	Sphene	Biotite	Ulvospinel	Pseudobrookite
Si	24.2	0.2	14.0	18.5		
Ti	0.1	0.0	21.2	3.8	11.4	39
Al	16.1	0.1	0.8	8.4	2.3	
Cr	0.0	0.0	0.0	0.0	0.0	
Fe	0.6	0.8	1.8	14.9	56.8	24
Mn	0.0	0.5	0.0	0.0	0.0	5 1
Mg	0.1	0.6	0.2	5.0	0.1	
Ca	9.6	39.6	20.5	0.3		
Na	2.5	0.2	0.2	2.0	4	
K	0.4	0.2	0.0	6.7		
Ca		12.5				
O^{b}	47.1	50.2	39.7	40.9	29.3	33
Sum	100.7	104.9	98.4	100.5	99.9	97

TABLE 1. MICROPROBE ANALYSES OF DIKE MINERALS

^a Estimated stoichiometrically by combining with Fe, Mn, Mg, and Ca in carbonate molecules. High sum implies that the analysis volume actually contained nearly pure calcite plus various silicate and oxide contaminants.

^b Estimated stoichiometrically, generally assuming Fe to be divalent except in the case of the ulvospinel analysis for which the Fe^{3+} : Fe^{2+} ratio was calculated, during successive reductions, by balancing Fe with the other cations in spinel-type formulas.

Analyst-J. S. Dickey, Jr.

Mineral Formulas

Plagioclase—An₆₇Ab₃₀Or₃

Calcite-CaCO3

Sphene-Ca1Ti 95Si1O5

Pseudobrookite—(Fe,Mg)Ti₂O₅

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Biotite (half cell)— $(Ti_{,43}Fe_{1.09}Mg_{,36})(Si_{2.73}Al_{1,27})(K_{,71}Na_{,36}Ca_{,03})O_{10}(OH)_2$ Ulvospinel-magnetite— $(2FeO \cdot TiO_2)_1(FeO \cdot Fe_2O_3)_1$

The biotite analysis is slightly erroneous in that it fails to account for H_2O (~4%) and has a slight deficiency of octahedral cations. Likewise, the pseudobrookite analysis sums to only 97 percent. Repeated attempts, using various instrument conditions, were made to analyze this phase; however, all attempts at quantitative analysis were thwarted by the minute thicknesses of the skeletons.

DISCUSSION

Phase equilibrium studies of the Fe-Ti oxides by MacChesney and Muan (1959) and by Taylor (1964) show that at magmatic temperatures ulvospinels, ilmenites, or ilmenites, pseudobrookites, are stable assemblages whereas ulvospinelss, -pseudobrookite.s. represents disequilibrium. The experiments of Speidel (1970) show that the addition of Mg to the Fe-Ti-O system at high $(>10^{-7} \text{ bars})$ oxygen fugacities results in the decomposition of the rhombohedral phase to an ulvospinels, phase and a pseudobrookite_{ss}, phase. Spinels in this experimental system, however, contain >10 percent MgO by weight before the rhombohedral phase disappears. Since this is not true of the analyzed spinel of Table 1, we conclude that crystallization of the Fe-Ti oxides in the dike occurred under disequilibrium conditions and, therefore, that it is impossible to assign approximate oxygen fugacity or temperature estimates to the crystallizing magma. Additional indications of disequilibrium show up not only in the variable plagioclase compositions, but also in the occurrence of skeletal apatite and the presence of the other oxides, rutile and hematite.

The fact that skeletal oxides and silicates are rarely observed in rocks is, to an extent, petrologically reassuring. If the data reported here are typical, the development of this texture is not only indicative of abnormal growth and temperature conditions, but almost as surely of chemical disequilibrium as well.

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