

# ON THE CRYSTALLIZATION OF ACCESSORY ZIRCON IN GRANITIC ROCKS OF MAGMATIC ORIGIN<sup>1</sup>

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## ABSTRACT

A solution to the problem of the time of crystallization of zircon in granitic magmas is attempted by examining the probable behaviour of the  $Zr^{4+}$  ion, according to its crystallochemical properties. It is suggested that within a single intrusion of granitic rock zircon crystallization is early (intratelluric) and is of short duration.

## INTRODUCTION

Two divergent views have been expressed on the time of crystallization of accessory zircon in granitic magmas. Some workers believe (*cf.* Wager & Mitchell, 1951, p. 192; Poldervaart, 1956) that zircon crystallizes early and within a short time (Poldervaart, 1956, p. 547). Others think that zircon crystallizes late (*cf.* Moorhouse, 1956). These opposite conclusions were supported by Larsen & Poldervaart (1957) and Moorhouse (1956) by employing similar methods *viz.* statistical studies of the incidence of zircon inclusions in different host minerals, in thin sections of rocks. The results from this approach are obviously inconclusive (*cf.* Moorhouse, 1956, p. 261) since they will be influenced by the choice of material and the admittedly erratic nature of zircon distribution in rocks.

In this paper an attempt is made to find a solution to the problem by resource to the crystal chemistry of zirconium in zircon and its probable behaviour during the crystallization of a granitic magma. The approach is admittedly theoretical; but it is based on established principles of crystal chemistry and known experimental data regarding the properties of the  $Zr^{4+}$  ion.

## GEOCHEMISTRY OF ZIRCONIUM IN GRANITIC ROCKS

Zircon ( $ZrSiO_4$ ), is the only zirconium mineral of geochemical importance (Rankama & Sahama, 1949, p. 565). Because of the small ionic radius (0.79 Å) and high charge (4), the  $Zr^{4+}$  ion cannot readily enter the structure of minerals by admission, substitution, or camouflage. Like other cations of small ionic radii and high charge (*e.g.*,  $Mg^{2+}$ ), the

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$Zr^{4+}$  ion prefers to form the stable nesosilicate zircon (*cf.* Ramberg, 1954, p. 268–270). This is also a consequence of the high electronegativity of the  $Zr^{4+}$  ion (1.4). Cations with high electronegativity values combine with silicate structures in which the electronegativity value of the oxygen is low (Ramberg, 1952, p. 354). This value is lowest in nesosilicate structures and consequently the  $Zr^{4+}$  ion naturally prefers to form the stable nesosilicate zircon.

The  $Zr^{4+}$  ion has a high ionization potential (34.0) which is a measure of anion affinity, "the power of free cations to attract anions" (Ahrens, 1953, p. 5). Because of its high valency the  $Zr^{4+}$  ion has a large  $E$ -value, the activation energy of migration of the ion (Wickman, 1943, p. 373). During the crystallization of silicate melts such cations tend to take up ordered positions with relative ease, and hence the mineral separates out at relatively high temperatures and the stability of the structures formed is high even at high temperatures (Wickman, 1943, p. 389). Because of the large  $E$ -value and high anion affinity of the  $Zr^{4+}$  ion, zircon formation is rapid and early during the crystallization of a silicate melt.

However, zircon does not crystallize early during the crystallization of a basaltic magma (Poldervaart, 1956, p. 524–525). This is explained in part as the result of the low concentrations (Wickman, 1943, p. 388) of zirconium in the magma, but may perhaps also be related to two other crystallochemical properties of the  $Zr^{4+}$  ion in zircon. The  $Zr^{4+}$  ion occurs in 8-co-ordination in zircon, which is unnatural to its size. Because of its small size, its co-ordination should lie on the border line between 6 and 8, closer to the 6-co-ordination side (Rankama & Sahama, 1949, p. 564). But zirconium takes up an 8-co-ordination because, with a lower co-ordination, it cannot form a simple silicate. During the crystallization of a basaltic magma, at relatively high temperatures (1100°C), the zircon structure is unstable. The stability of the structure is also decreased because of the strong contrapolarization effect of the small highly charged  $Zr^{4+}$  ions which loosens the cohesion with the  $SiO_4$  groups (*cf.* Eitel, 1954, p. 31 and 803). However, the ubiquitous presence of zircon crystals in magmatic granites, implies that these factors do not prevent the formation of the mineral as a stable phase during the crystallization of granitic magmas presumably because of the higher concentrations of the  $Zr^{4+}$  ions and the lower temperatures (700°–800°C) of these magmas.

Zircon which occurs in conspicuously minor amounts is the only nesosilicate in magmatic granites. The characteristic feature of granite crystallization is the formation mainly of feldspars and quartz (tectosilicates) and minor amounts of the accessories biotite (phyllosilicate)

and/or hornblende (inosilicate). The predominance of minerals with 3-dimensional framework structures and chains and the insignificant amounts of nesosilicate is probably the result of oxygen deficiency in granitic magmas. This is apparently due to the relatively high content of silicon and aluminium whose valency demands can be met only by sharing the oxygen available in the magma. It is logical to conclude, therefore, that discrete  $\text{SiO}_4$  tetrahedral units, necessary for the formation of nesosilicates are likely to exist *before* the onset of the main period of crystallization. Hence favorable conditions for the formation of zircon are more likely to exist in the very early stages of crystallization of granitic magmas rather than during the later stages.

It is known that diadochic replacement of large ions for smaller ions takes place more readily at high temperatures. In zircons small amounts of  $\text{U}^{4+}$  (0.97 Å) and  $\text{Th}^{4+}$  (1.02 Å) are invariably present probably substituting for  $\text{Zr}^{4+}$  (0.79 Å). Since there is a 23 and 29 per cent difference respectively in the ionic radii of  $\text{U}^{4+}$  and  $\text{Th}^{4+}$ , compared with that of the  $\text{Zr}^{4+}$  ion, the inference is strong that the substitution of the larger ions took place at high temperatures. This adds further weight to the probability that zircon crystallized early in granitic magmas when high temperatures prevailed.

There is another geochemical feature of the  $\text{Zr}^{4+}$  ion which suggests that zircon cannot crystallize as a late mineral in granitic magmas. Highly charged ions such as  $\text{Zr}^{4+}$  can form hydrated complexes (zirconates,  $(\text{Zr}(\text{OH})_8)^{4-}$ ) and this tendency increases with increasing ionization potential and decreasing temperature (Goldschmidt, 1954, p. 45). During progressive crystallization of granitic magmas temperatures decrease and water concentrations increase (*cf.* Smith, 1948, p. 536). The  $\text{Zr}^{4+}$  ion is unlikely to crystallize as the anhydrous nesosilicate zircon in the presence of water which has a strong polarizing influence (Wickman, 1943, p. 394). In granitic rocks hydrated complex zirconium silicates such as eudialite  $[(\text{Na}, \text{Ca}, \text{Fe})_6\text{ZrSi}_6\text{O}_{18}(\text{OH}, \text{Cl})?]$ , and catapleite  $(\text{Na}_2\text{Zr}[\text{Si}_3\text{O}_9] \cdot \text{H}_2\text{O})$  are absent. It is therefore most probable that zircon, the anhydrous nesosilicate of zirconium, crystallizes in the early stages of crystallization of granitic magmas when water was not separated as a separate phase.

Euhedral zircon crystals of volcanic rocks, which in many cases show magmatic corrosion, suggest that zircons crystallized in the intratelluric stage. Similar zircon suites with similarly reduced major axes have been noted by Alper & Poldervaart (1957), and Folinsbee & Ritchie (1957) for intrusive equivalents of the extrusives, suggesting that, in both, zircon crystallized during the intratelluric stage. The most favorable conditions for the crystallization of nesosilicate zircon exist during the

intratelluric stage when formation of framework structures has either not begun or is only in the initial stages. Zircon crystallization is probably rapid since the  $Zr^{4+}$  ion has high anion affinity, and tends to take up ordered positions with relative ease at relatively high temperatures. It is suggested, therefore, that the crystallization of zircon in granitic rocks is of short duration, completed immediately after the emplacement of the magma from its source and prior to the crystallization of the other minerals.

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