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ZIRCON STABILITY AND THE ZrO_2 - SiO_2 PHASE DIAGRAM

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INTRODUCTION

The compound $ZrSiO_4$ makes up 98 percent or more, by weight, of the mineral zircon. In view of the petrological and technological importance of this mineral, accurate information on the thermal stability of $ZrSiO_4$ is highly desirable. Yet even in the most recent studies there is no general agreement as to the temperature or the manner of breakdown of $ZrSiO_4$. Table 1 lists the stability data of various investigators.

The uncertainty regarding the thermal stability of $ZrSiO_4$ is reflected in the published phase diagrams for the system ZrO_2 - SiO_2 . Thus far, three fundamentally distinct configurations have been presented. The diagrams of Washburn and Libman (1920) and of Zhirnowa (1934) depict zircon as a congruently-melting compound, the melting point being given

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TABLE 1. DATA ON THE THERMAL STABILITY OF $ZrSiO_4$

Investigators	Year	Manner of Breakdown	Temperature
Washburn and Libman	1920	congruent melting	2550°C
Zhirnowa	1934	congruent melting	2430°C
Geller and Lang	1949	incongruent melting	1775°C
Curtis and Sowman	1953	solid state decomposition	1540°C
Cocco and Schromek	1957	incongruent melting	1720°C

as 2550°C and 2430°C, respectively. In contrast, the diagrams of Geller and Lang (1949) and Cocco and Schromek (1957) show zircon melting incongruently at 1775°C and 1720°C, respectively, the eutectic being set by Geller and Lang at 1675°C. Finally, Curtis and Sowman (1953) represent zircon as decomposing in the solid state at 1540°C, some 135 degrees below the zirconia-silica eutectic. The situation is further complicated by lack of agreement as to the role of liquid immiscibility, of solid solution in zirconia-rich compositions, and of polymorphic inversion in the zirconia end-member. Of two recent phase diagram compilations, one (Levin, Robbins and McMurdie, 1964) presents two of the above conflicting diagrams, and the other (Morey, 1964) gives no diagram for the system.

Results of some recent studies by the present authors (Butterman, 1965; Beard, Bradley, Butterman and Foster, 1965) permit a reasonable resolution of most of the earlier conflicting data. Confirmation has been received from theoretical and experimental data of other current investigations (Rosen and Muan, 1965; Muan, pers. comm., 1965; Jones, Kimura, and Muan, 1966). The purpose of the present note is to incorporate these and other recent data in a ZrO_2SiO_2 phase diagram believed to be more accurate than any previous diagram.

EXPERIMENTAL METHODS AND DATA

Materials used in this study included spectroscopically pure Wah Chang zirconia, Zircoa purified hafnia-free zirconia, Cabosil amorphous silica, General Electric pure synthetic quartz, high-purity Malvern "novacite" silica, purified natural zircon, and synthetic $ZrSiO_4$ prepared from the foregoing pure oxides. The heat-treatment of pellets or platinum foil-wrapped powders of these materials was carried out in a horizontal Heraeus rhodium-wound tube furnace, a vertical Tem-Pres platinum—rhodium quenching furnace, or an iridium-ribbon strip-furnace. Temperatures were determined with a Pt94-Rh6/Pt70-Rh30 thermocouple placed in contact with the sample, or with an optical pyrometer sighted on the sample, and calibrated with reference to the thermocouple. Crystalline phases were identified by means of a Norelco high-angle diffractometer.

About two dozen runs were made to establish the manner and the temperature of decomposition of pure zircon, by determining the highest temperature at which the oxides combined to yield zircon, and the lowest temperature at which preexisting zircon decomposed to yield the oxides. Samples for this purpose were prepared from ZrO_2 and SiO_2 in the stoichiometric proportions of $ZrSiO_4$. The results of the more definitive runs, appear in Table 2.

TABLE 2. SELECTED DATA ON SYNTHESIS AND STABILITY OF ZIRCON

Temperature (°C)	Time (hrs)	Effect on Zircon Development
Starting Material: Unreacted ZrO_2 and SiO_2		
1669	17	pronounced $ZrSiO_4$ development
1683	13	no $ZrSiO_4$ developed
1705	13	no $ZrSiO_4$ developed
Starting Material: Partially reacted ZrO_2 and SiO_2 , containing appreciable $ZrSiO_4$		
1666	17	appreciable increase in $ZrSiO_4$
1669	5	appreciable increase in $ZrSiO_4$
1685	4	noticeable decrease in $ZrSiO_4$

The above results indicate that the upper limit of stability lies between 1669° and 1683°C. A recent thermodynamic calculation (Rosen and Muan, 1965) suggests that zircon is stable to approximately 1600° to 1650°C, and some experimental tests similar to our own (Muan, 1965) place it between 1670° and 1685°C. Strong confirmation is thus given to the $1676 \pm 7^\circ C$ value of the present study, rather than to any of the values listed in Table 1.

In the present study it was found that the upper limit of stability of zircon and the minimum temperature of liquid formation in the ZrO_2 - SiO_2 system are less than 10 degrees apart. This circumstance renders it very difficult to determine whether zircon melts incongruently a few degrees above the zircon-silica eutectic, or whether it decomposes in the solid state a few degrees below the zirconia-silica eutectic. A decision was finally rendered in favor of the second alternative. The data in Table 3, obtained on a mixture of 10 percent zircon and 90 percent cristobalite (by weight), are typical of the results on which this decision is based. On the basis of such results it is concluded that the zirconia-silica eutectic lies at approximately $1687 \pm 4^\circ C$, and therefore about 10 degrees higher than the maximum temperature of zircon stability. Muan's (1965) finding that the eutectic is slightly (perhaps 5°) higher than the zircon decomposition temperature is considered to be in excellent agreement for studies in this

TABLE 3. DATA ON THE MANNER OF DISSOCIATION OF ZIRCON

Temperature (°C)	Time (hrs)	Observations
1663	3	unsintered, with no zircon decomposition
1683	3	unsintered; zircon partially decomposed
1691	3	compact, fused mass largely composed of zirconia and glass

temperature range. Likewise, Rosen and Muan (1965) concluded that $ZrSiO_4$ decomposes to ZrO_2 plus SiO_2 slightly below the eutectic temperature.

PROPOSED ZrO_2 - SiO_2 PHASE DIAGRAM

A proposed new phase diagram for the system ZrO_2 - SiO_2 incorporating the findings summarized in Tables 2 and 3, is presented in Figure 1. Certain additional features of the diagram, based largely on the recent work of other investigators, and believed to render the diagram more acceptable than previous versions, deserve comment.

Although Barlett (1932) detected evidence for liquid immiscibility in melts of the ZrO_2 - SiO_2 system, no effort was made to incorporate this phenomenon in the phase diagram until the diagram of Toropov and Galakhov (1956), which showed a two-liquid region between 41 and 62 percent (by weight) of silica, with a lower limit of 2250°C. Glasser, Warsaw and Roy (1960) on theoretical grounds suggested a hypothetical diagram involving a two-liquid region between 10 and 53 mol percent of silica, thus embracing the 1:1 mol ratio corresponding to $ZrSiO_4$. To test this possibility five samples of purified natural zircon were fired in the iridium strip furnace between 2250°C and 2400°C for periods up to one minute. No liquid immiscibility was observed. On the other hand, a mixture of 50 percent ZrO_2 and 50 percent SiO_2 (by weight) fired at about 2350°C for 30 seconds displayed well-developed immiscibility. Accordingly, the more restricted immiscibility range proposed by Toropov and Galakhov (1956) has been adopted in Figure 1. One feature commonly omitted from earlier diagrams involves polymorphic inversions in the zirconia and silica end-members. The well-known inversions in silica at 573°, 867° and 1470° are included. Retention of the 867°C and 1470° inversions is based on the results of recent studies (Roy and Roy, 1964; Rockett and Foster, 1966) supporting the view that tridymite is a true polymorph of silica. The inversion temperatures of monoclinic to tetragonal zirconia at 1170°C, and of tetragonal to cubic zirconia at 2285°C, are based on the findings of Mumpton and Roy (1960) and of Smith and Cline (1962), respectively.

One remaining feature of the diagram, the absence of solid solution at

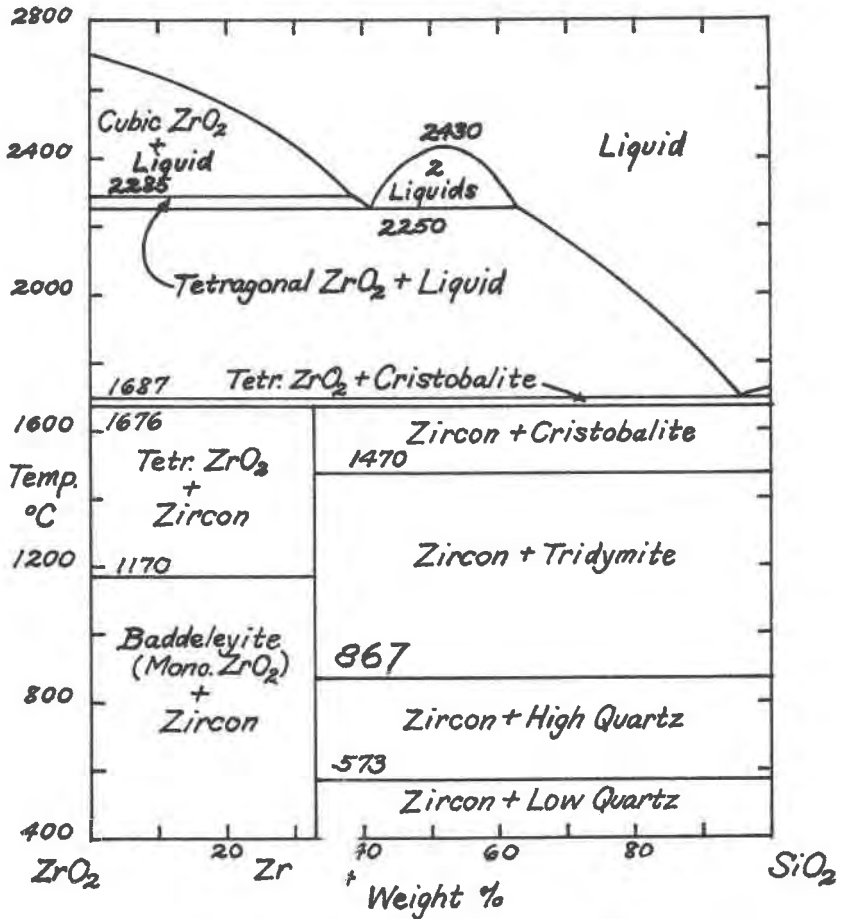


FIG. 1. Proposed phase diagram for ZrO_2 - SiO_2 system.

the ZrO_2 -end of the system, requires comment. The diagrams of Zhirnowa (1934), Geller and Lang (1949), Curtis and Sowman (1953) and Toropov and Galakhov (1956) have all featured solid solution extending from pure zirconia to the extent of 3 to 10 percent silica. This solid solution effect does not appear to have been founded on very clear evidence, and recent work by Keler and Andreeva (1962) has cast considerable doubt on its validity. Later studies by Lang, Franklin and Tylutki (1965) suggest that the solid solution in ZrO_2 does not exceed 0.1 percent SiO_2 (or 0.3 percent $ZrSiO_4$). For all practical purposes, then, solid solution effects may be ignored.

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