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SOLUBILITY AND SOLVATION REACTIONS OF QUARTZ IN DILUTE HYDROTHERMAL SOLUTIONS

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ABSTRACT

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Equilibrium solubilities of quartz in both the SiO_2–H_2O and SiO_2–H_2O–NaOH systems have been measured along the three-phase subcritical curve at temperatures up to 325°C. The solubility data show that quartz dissolves primarily as a monomeric aqueous species and that sodium–silica complexing is of no analytical importance under these conditions. A model has been devised which predicts silica solubility as a function of NaOH concentration in this three-phase, three-component system. A reinterpretation of pre-existing quartz-solubility measurements in the SiO_2–H_2O–Ar system has yielded a value of 4.2 for the hydration number of the aqueous silica complex at 1,000 bars total pressure and 500°C. A new treatment of earlier solubility measurements in the system SiO_2–H_2O–Na_2S has shown that sulfide-bearing silica complexes may not be of any quantitative significance at 150°C at the vapor pressure of the system.

INTRODUCTION

Geochemists have displayed an increasing interest in solubility studies pertinent to natural hydrothermal systems. These natural solutions are highly complex, and preliminary experimentation may only generally be carried out over a range of limiting, simplified systems. Necessary fundamental data such as the nature of specific constants are usually most readily obtained only through investigation of simple systems. The gradual accumulation of such thermodynamic information allows increasingly comprehensive studies of complicated natural solutions.

The systems SiO_2–H_2O and SiO_2–H_2O–NaOH were selected for study partly because of the observed alkalinity and sodium content of many natural hydrothermal solutions and the ubiquity of hydrothermal silica deposits, and partly because of the considerable amount of experimental data on these two systems, which facilitate theoretical interpretations. However, the data presented herein are of interest not so much because of any similarity between the experimental solutions and natural hydrothermal solutions, but

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Chem. Geol., 8 (1971) 107–122

because they allow tests to be made for polymerization and for the presence of sodium–silica complexing, features which, if present, would greatly affect all subsequent theoretical treatments of silicate-bearing solutions.

A re-interpretation of the solubility data of Dickson (1966) and Sommerfeld (1967) is also included, which bears on the hydration number of the aqueous silica complex and on the possibility of a sulfide-bearing silica species in aqueous solutions of Na_2S.

The main body of the present work may be considered a continuation of the research presented by Anderson and Burnham (1967), which consisted chiefly of quartz and corundum solubility measurements in supercritical aqueous chloride and hydroxide solutions. They proposed several possible quartz solvation mechanisms at that time, but lack of the relevant thermodynamic information still prevents thorough quantitative or theoretical treatments of such supercritical systems today. However, the necessary background data do exist over limited portions of the boiling curves of pure water, and H_2O–NaOH, H_2O–SiO_2 and H_2O–H_2S systems, thus permitting preliminary quantitative treatment in the subcritical range.

PREVIOUS WORK

The solubility of quartz in pure water along the lower three-phase region (coexisting quartz, aqueous solution and vapor), has been previously established by four independent studies: Kennedy (1950), Kitahara (1960a), Morey et al. (1962) and Siever (1962). These results are compiled in Fig. 1 along with the solubility measurements of the present study.

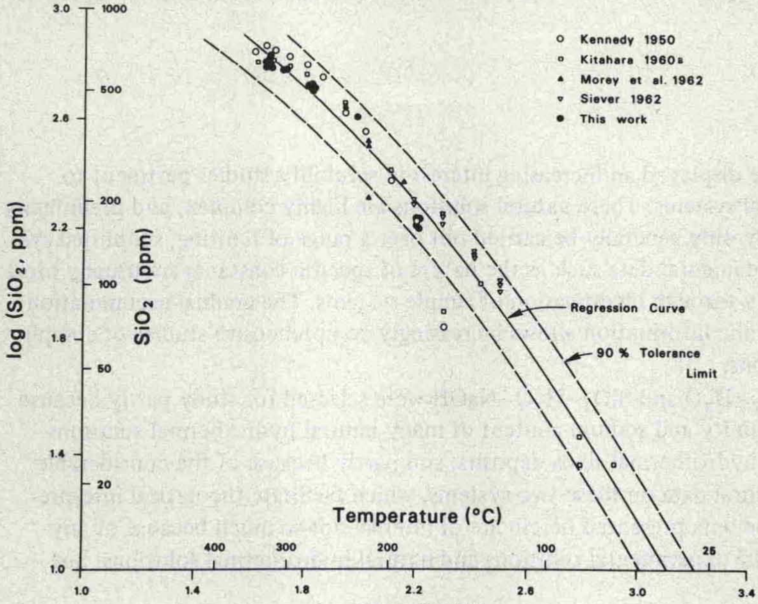

Fig. 1. Least squares quadratic fit to all published solubility data for the three-phase subcritical region of the quartz–water system up to 325°C.