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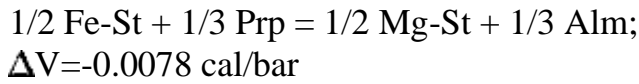
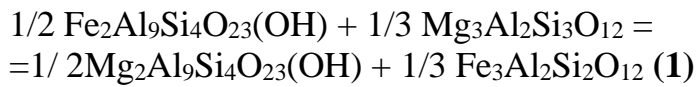
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Fed'kin V.V., Aranovich L.Y., and Yakovleva L.Yu. Staurolite - garnet exchange equilibrium: experiment, calculations, and application.

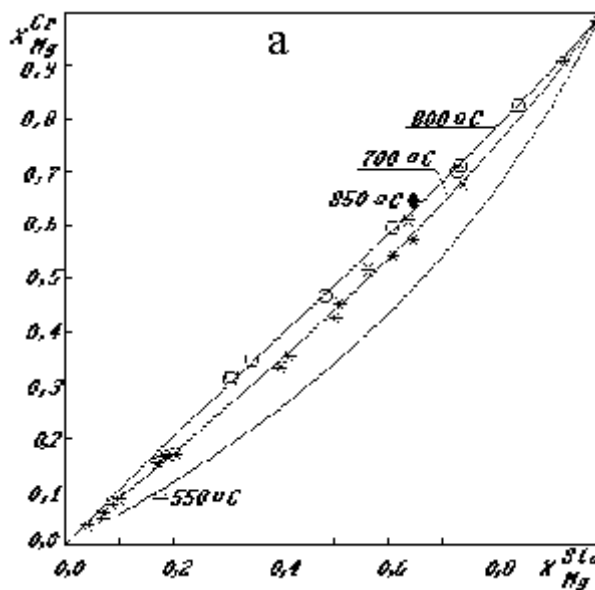
The Fe-Mg exchange equilibrium between staurolite and garnet



was carried out at T=700 and 800°C, P=4-30 kbars, the Ni-NiO oxygen buffer, using hydrothermal, gas and solid-media apparatus [1]. Controls were run at 550°C and 850°C and resulted in good thermodynamic agreement with the available detailed data for the 800 and 700°C isotherms.

The experiments were done over a wide range of coexisting phase compositions, with excess water or oxalic acid and additions of NH₂Cl and Fe. Run durations were 3-14 days. Reproducibility of results from runs of different duration, attainment of equilibrium from the two sides, and the wealth of experience with the garnet-involving Fe-Mg exchange equilibria strongly suggest that the obtained data approach closely the equilibrium conditions. In addition, there is also indirect evidence for the runs having attained thermodynamic equilibrium, such as release of the impurity species (Ca from Gr, Zn from Sta) from the coexisting phases. Natural and synthetic minerals were used as starting materials in the St-Grt exchange equilibrium studies. The natural samples and run products were carefully analyzed chemically and by the electron microprobe "Camebax" fitted with the energy-dispersion unit Link.

Experimental results for exchange equilibrium (1) as well as natural data on Fe-Mg distribution between St and Grt are presented in Fig.1.



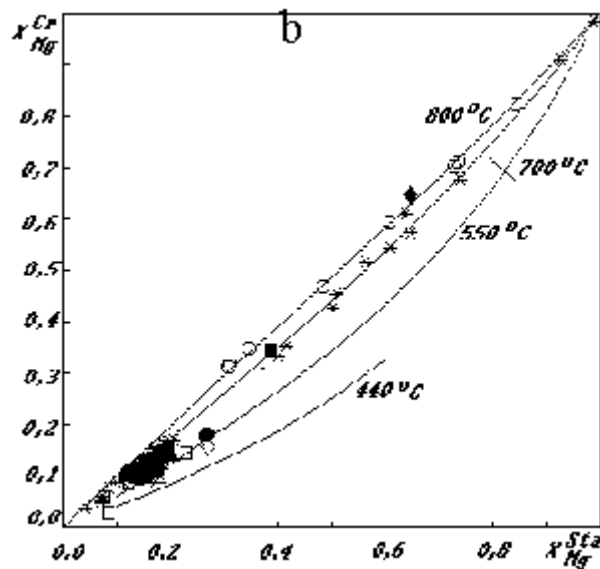


Fig.1. **Experimental results on the Fe-Mg exchange equilibrium between St and Grt; a** - approximation of experimental results by the Least Square Method; **b** - area of St and Grt coexisting compositions from natural assemblages and from experiment.

15

The experimental data cover the whole range of the coexisting St and Grt ($X_{Mg}=0.04-0.99$), thus providing an advantage over the natural ratios, because a more complete and accurate account can be taken of the effect produced by the compositions of phase on the distribution of isomorphous components. On the other hand, the natural material covers a wider temperature range of the stability of the St-Grt assemblage, 435-730°C, reflecting the more realistic and widespread compositions of the coexisting St and Grt. Consequently, experimental and petrologic observation well complement each other and their thermodynamic treatment was performed with due regard for these singularities.

For staurolite solid solution a regular mixing model of Fe-, Mg- and Zn-components has been assumed [2]. The experimental data on St-Gr exchange equilibria were approximated by the Least Square Method and were described by equation:

$$T = (3851 + 7.8P + 384(X_{Fe} - X_{Mg})^{St}) / (R \ln K_D + 3.639 + 0.563(X_{Fe} - X_{Mg})^{St}) \quad (2)$$

Since neither St nor Grt in experimental samples contained impurity components Ca and Zn, equation (2) best describes the experimental results: $K=0.971$; $\sigma = \pm 52$ cal ($\pm 14^\circ\text{C}$), but it differs from the one for natural assemblages [2], especially with regard to the parameters of Fe-Mg interaction in staurolite. Simultaneous treatment of natural and experimental data was performed with the experimentally derived enthalpy and entropy changes of reaction (1) as a more reliable and corresponding to a wider compositional range of coexisting phases. On the other hand, the excess energies of

staurolite were corrected slightly after recalculation and St-Grt geothermometer equation has been derived:

$$T = \frac{(3851 + 7.8P + 5704X_{Ca}^{Grt} + 253(X_{Fe} - X_{Mg})^{St} + 1741X_{Zn}^{St})}{(1.9871 \ln KD + 3.639 + 1.242X_{Ca}^{Grt} + 1.38(X_{Fe} - X_{Mg})^{St} + 3.702X_{Zn}^{St})}$$

This equation ($K = 0.956$; $\sigma = \pm 116$ cal; $t = \pm 27^\circ\text{C}$), takes into account both the Ca-correction in garnet and Zn-correction in staurolite and seems to be best suited to the purposes of mineralogical geothermometry.

References:

1. Fed'kin V.V., Yakovleva L.Yu. Staurolite-garnet exchange equilibrium: experiment, calculation, application. // *Experiment in Geosciences*, 1993. V.2, N.2, pp. 1-11.
2. Fed'kin V.V., Aranovich L.Ya. The empirical refinement of the staurolite-garnet geothermometer. // *Experiment-89*, Moscow: Nauka, 1990. pp.41-44.

Yakovleva L.Yu. Experimental study on the mechanism and kinetics of the reactions in the model system St+Q+Grt+Sil+H₂O.

The experimental study on the mechanism and kinetics of the reactions in the model system $\text{St}+\text{Q} \leftrightarrow \text{Grt}+\text{Sil}+\text{H}_2\text{O}$ has been carried out. It was found that the garnet crystallization is limited by the concentration of silicate components in the solution, which is in turn dependent on the St, Qtz, and Sil solubility. The highest solubility of these minerals with favorable Al:Si ratio is attained in a water-carbonic acid-chloride fluid in the temperature range $700\text{-}800^\circ\text{C}$ ($P=5\text{ kbar}$). At lower temperatures garnet crystallization does not occur and at higher temperatures high alumina phases - spinel or corundum form. It was determined experimentally (at $T=700^\circ\text{C}$ and $P=5$ kbar) that staurolite solubility in a complex water-carbonic acid-chloride fluid is higher than in oxalic acid and saturation concentration in the experiment cannot be reached even in 15 days. A method of stage accretion of edges of garnet of different composition on the starting seed has been proposed to model the zoning in garnet. The analysis of experimental data showed that concentrational garnet zoning is a growth one and its appearance is connected with the processes of solubility-crystallization on the crystal-solution interface.

References:

1. Yakovleva L.Yu., Fonarev V.I. (1996) Features of mechanism and kinetics of garnet crystallization (experimental data). // *Experiment in Geosciences*, V.5, N.1.