

SHI Xunli and HU Jiawen 2013. Calculation and thermodynamic analysis of $\log(O_2)$ - $\log a(SiO_2)$ diagrams of the CaO-FeO-SiO₂-O₂ system *Acta Geologica Sinica* (English Edition), 87(supp.): 768-770.

Calculation and thermodynamic analysis of $\log(O_2)$ - $\log a(SiO_2)$ diagrams of the CaO-FeO-SiO₂-O₂ system

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Key words: phase diagram configuration, one-grade multisystem, magnetite, andradite, fayalite, kirschsteinite, hedenbergite

The phenomena of magnetite (Mt, Fe₃O₄), andradite (Andr, Ca₃Al₂Si₃O₁₂), hedenbergite (Hd, CaFeSi₂O₆) exsolved from or intergrown with Ca-Fe-rich olivines that may be fayalite (Fa, Fe₂SiO₄), or kirschsteinite (Kst, CaFeSiO₄), or their solid solutions have been found in many different geological settings, especially in Mg-poor cases. The relevant mineral assemblages often contain very pure wollastonite (Wo, CaSiO₃), or Ca-rich pyroxene (such as augite), and sometimes intergrow with hematite (H, Fe₂O₃). In order to understand the geochemical behaviors of these minerals and their physicochemical conditions, it is necessary to get accurate phase diagrams of the relevant systems under different conditions. At present, there are many theoretical and experimental reports on the phase equilibria of these systems (Hu et al., 2011; Selleby, 1997; Sommacal, 2004), but they are all defective somewhat. For instance, owing to the lack of thermodynamic data of minerals, some studies were only qualitative or semi-quantitative (e.g. Kst) (Hu et al., 2011), even one or some phases or components mentioned above were not involved. What is more, some data of different precisions or reliabilities were simply used together in calculation. Considering the data from different sources may be inconsistent with each other, some results may be problematic. Recently, Sommacal (2004) optimized the data of Kst with the model of Holland and Powell (1998). This dataset of Kst and that of other minerals or components by Holland and Powell (1998), as well as the Fa-Kst solid solution model of Mukhopadhyay and Lindsley (1983), are adopted to calculate $\log(O_2)$ - $\log a(SiO_2)$ diagrams under different temperatures and pressures.

For a $\log(O_2)$ - $\log a(SiO_2)$ phase diagram of the CaO-

FeO-SiO₂-O₂ system under given temperature and pressure, $f(O_2)$ and $a(SiO_2)$ are essentially external condition variables that define the stability fields of mineral assemblages, so O₂ and SiO₂ can be removed by projecting the phase composition space (i.e. chemography) of the quaternary system from SiO₂ and O₂ to the subspaces without SiO₂ and O₂, respectively (Hu, 2012; Hu et al., 2011), or can be eliminated together by matrix projection (Greenwood, 1975). As a result, the quaternary system is actually equivalent to a binary system in phase diagram topology (Hu, 2012). At given temperature and pressure, the CaO-FeO-SiO₂-O₂ system has four phases in an invariant assemblage, and three phases in a univariant assemblage. In this work, all phase assemblages are labeled with their absent phases (Zen, 1966). For simplicity, the invariant points and univariant lines corresponding to the above assemblages are also labeled with the same symbols, respectively. According to the topological analysis theory of phase diagrams, if m extra phases are added to an invariant assemblage, it will result in form an m -grade (or m -level) multisystem (Hu et al., 2004; Hu, 1998).

The main steps of the phase diagram calculation can be summarized as follows:

Firstly, calculate the univariant lines. Balance each univariant reaction defined by its univariant assemblage, and express it in standard form which means the form as “ $0 = \sum v_B$ ”, where v_B is the stoichiometric number of phase or component B in a reaction (which is negative for reactant, and positive for product). The molar Gibbs free energy (relative value) of every mineral or component can be calculated with the model of Holland and Powell (1998). The calculation of every univariant line is based on its corresponding chemical equilibrium condition. The calculated values of $\log a(SiO_2)$ and $\log f(O_2)$ are used to plot the $\log a(SiO_2)$ - $\log f(O_2)$ diagrams.

Secondly, discriminate the stable fields of reactant or product assemblages. For the $\log(O_2)$ - $\log a(SiO_2)$

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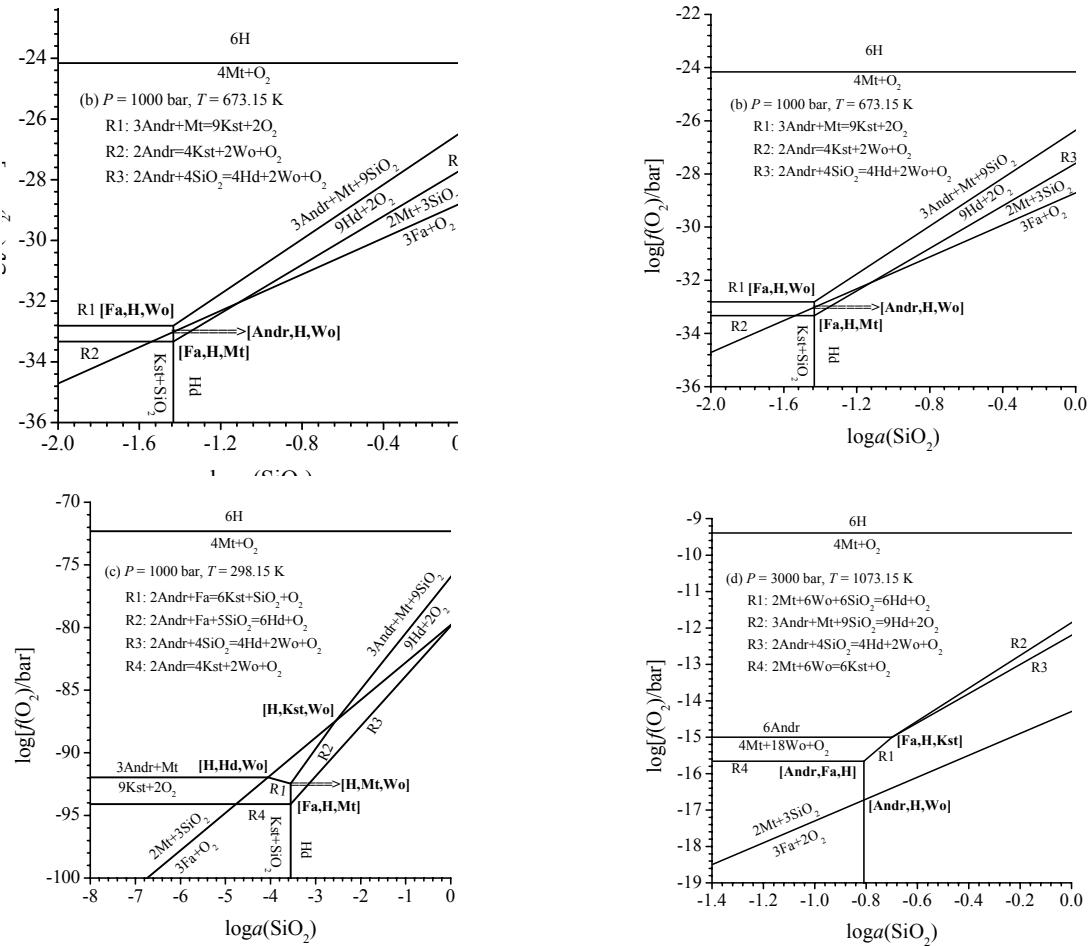


Fig. 1. $\log(f(O_2))$ - $\log(a(SiO_2))$ diagrams of $CaO-FeO-SiO_2-O_2$ system under constant temperatures and pressures.

diagrams in this work, almost all univariant reactions involve O_2 or SiO_2 , or both of them. According to La Chaterlier's principle, the mineral assemblages on the side of O_2 or SiO_2 can only be stable on the lower $f(O_2)$ or $a(SiO_2)$ side.

Thirdly, determine the stable parts of the univariant lines. According to Schreinemakers' rules (Zen, 1966) and the results in the second step, if the reactant or product assemblage of an arbitrary reference univariant line contains phase B and is stable on one side of the univariant line, then the phase B-absent univariant line belonging to the same invariant assemblage can only be stable on the opposite side of the reference univariant line.

Finally, determine the stabilities of invariant points. According to the closed net theory of multisystems (Hu et al., 2004; Yin et al., 2002; Zen, 1966), the invariant points of a one-grade multisystem cannot be all stable under any given conditions. According to the stability theory of invariant points (Cheng and Greenwood, 1990; Hu et al., 2000; Lépine et al., 1992; Vielzeuf and Boivin, 1984), if an invariant point is passed through by the metastable part of a univariant line emanating from the invariant point, the

invariant point and the univariant lines emanating from it must be all metastable.

The seven-phase system (a three-grade multisystem) in this work includes one-grade multisystems. Therefore, it would be very time consuming if we do all the above thermodynamic calculations and discriminations for each one-grade multisystem. We found a high-efficiency approach: (1) Choose an arbitrary one-grade multisystem as the initial system, do all the foregoing calculations and discriminations associated with reactant and product assemblages, univariant lines and invariant points; (2) Add a new phase to the system, and repeat the above calculation and discrimination for all one-grade multisystems that do not include the metastable invariant assemblage(s) determined in the preceding step. Finally, put all the stable parts of univariant lines together to form a complete phase diagram. In this way, a complete stable equilibrium phase diagram can be obtained with a small amount of calculation (Figure 1).

Through systematic analysis of the calculated phase diagrams, the following conclusions can be drawn: (1) Under given temperature and pressure, if $f(O_2)$ is high

enough, Fa and Kst will change into minerals that are more oxidizing and/or richer in silica; at higher $a(\text{SiO}_2)$, the silica-rich minerals are more stable. (2) Temperature has much more notable influence on reaction equilibria than pressure. At constant pressure, as temperature drops, univariant lines and invariant points dramatically move towards to the direction of lower $f(\text{O}_2)$ or $a(\text{SiO}_2)$. The drop of temperature can drive oxidation reactions, and the SiO_2 released from oxidation reactions can further drive some SiO_2 -consuming reactions. Consequently, if temperature is low enough, Fa and Kst will spontaneously transform into oxidizing minerals or silica-rich minerals. These facts suggest that all reactions in the calculated phase diagrams have significant changes in entropy, because they involve O_2 or SiO_2 , or both of them. (3) It is found that the phase diagrams of one-grade multisystems {Fa, H} and {Wo, H} can change their configurations with temperature below the highest phase separation temperature (about 1040 °C) of Fa-Kst solid solution. The most attractive features of these changes are that the changes always happen in one-grade multisystems, and the relatively stable net and relatively metastable net of a one-grade multisystem always *simultaneously* change their stabilities as a whole. That is, if the relatively stable net becomes metastable, then the relatively metastable net will also become metastable. In The seven-phase system in this work undergoes two configurational transformations, which result in three configurations (Fig. 1). (4) Pressure has no remarkable influence on the positions of most reaction equilibrium lines, except for few ones. Nevertheless, the increase of pressure can raise the configurational transformation temperatures of phase diagrams, which has same effect as temperature decrease do, but not as notable as it.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos 41172118, 40873018, 90914010), and the Natural Science Foundation of Hebei Province (Grant No. D2012403010).

References

- Cheng, W. and Greenwood, H.J., 1990. Topological construction of nets in ternary $(n+3)$ -phase multisystems, with application to $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ and $\text{MgO}\text{-SiO}_2\text{-H}_2\text{O}$. *Canadian Mineralogist*, 28(2): 305–320.
- Greenwood, H.J., 1975. Thermodynamically valid projections of extensive phase relations. *American Mineralogist*, 60(1-2): 1–8.
- Holland, T.J.B. and Powell, R., 1998. An internally consistent thermodynamic data set for phases of petrological interest. *Journal of Metamorphic Geology*, 16(3): 309–343.
- Hu, J., Yin, H. and Duan, Z., 2004. A new method for the derivation of the closed nets in the phase diagram space of multisystems. I. The Absent Phase Substitution Method. *Journal of Metamorphic Geology*, 22(5): 413–425.
- Hu, J.W., 1998. *Improvement of theorem and method for the computer plotting of multisystem phase diagrams*. Science Thesis, Chengdu University of Technology, Chengdu, China, 52 pp.
- Hu, J.W., 2012. A general thermodynamic analysis and treatment of phases and components in the analysis of phase assemblages in multicomponent systems. *Science China—Earth Sciences*, 55(8): 1371–1382.
- Hu, J.W., Mao, S.D., Du, G.Q., Wu, Y.X. and Zhang, P., 2011. A new thermodynamic analysis of the intergrowth of hedenbergite and magnetite with Ca-Fe-rich olivine. *American Mineralogist*, 96(4): 599–608.
- Hu, J.W., Yin, H.A. and Tang, M.L., 2000. A simple, universal theory and method for computer-plotting of phase diagrams of a multisystem—SFM method. *Science in China Series B—Chemistry*, 43(2): 219–224.
- Lépine, L., Provost, A. and Vielzeuf, D., 1992. Stability sequence along univariant lines in system of $(C+N)$ phases. *Comptes Rendus de l'Académie des Sciences de Paris*, 314(2): 1463–1468.
- Mukhopadhyay, D.K. and Lindsley, D.H., 1983. Phase relations in the join kirschsteinite (CaFeSiO_4) - fayalite (Fe_2SiO_4). *American Mineralogist*, 68(11-12): 1089–1094.
- Selleby, M., 1997. An assessment of the Ca-Fe-O-Si system. *Metallurgical and Materials Transactions B*, 28(4): 577–596.
- Sommacal, S., 2004. *Computational petrology: Subsolidus equilibria in the upper mantle*, The Australian National University, Canberra, 284 pp.
- Vielzeuf, D. and Boivin, P., 1984. An algorithm for the construction of petrogenetic grids: Application to some equilibria in granulitic paragneisses. *American Journal of Science*, 284: 760–791.
- Yin, H.A., Hu, J.W., Tang, M.L. and Han, W.X., 2002. *The Phase Diagrams of Multisystems*. Beijing: Peking University Press, 203 pp.
- Zen, E.-A., 1966. Construction of pressure-temperature diagrams for multicomponent systems after the method of Schreinemakers: A geometric approach. *U. S. Geological Survey Bulletin* 1225: 1–56.