THERMODYNAMIC RESEARCH OF JADEITE-JADE AT HIGH TEMPERATURES AND HIGH PRESSURES BASED ON PHASE BALANCE INTELLIGENT CALCULATION

by

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Based on the thermodynamic calculation of chemical composition and the intelligent calculation of phase equilibria, the temperature-pressure of the diagenetic environment of Burma jadeite-jade was studied, and its metamorphism was verified. Firstly, the W_{kj} value and activity of the four end-member of jadeite (Jd), augite (Acm), diopsite (Di), and hedenbergite (Hed) were calculated. Jadeite rock system was simplified as NCFMASH, and the equilibrium temperature-pressure conditions of both the combination of quartz and jadeite, sodium-feldspar with little kyanite, and the combination of jadeite diopside, hedenbergite, kyanite, sodium-tremolite, tremolite and oblique zoisite were revealed as 751 °C with 17.0 kb, and 631 °C with 18.8 kb. Based on the two kinds of mineral combination with a small amount of sodium mica [Pa], the balance of the system temperature should be in the range from 700-770 °C, and balanced pressure-range should be in the range from 17.34-18.83 kb, which reflects the pure NCFMASH system hard rock type jadeite-jade rock formation of the real balance temperature-pressure range. It is concluded that the metamorphism of jadeite rock has a stable growth equilibrium temperature-pressure range, which is the reaction interval of the closed system NCTNASH. It is explained that the reason that synthetic jadeite-jade reaches the gem level is that it has not been simulated as a mineral assemblage in the later stage and it will be subjected to multi-phase dynamic metamorphism after the rock forms, so it is unreasonable that jadeite synthesize is not just from one mineral crystals.

Key words: *end-member activity calculation, temperature-pressure condition, phase balance intelligent computation, jadeite*

Introduction

The formation of rocks has always been one of the focuses of geologists, besides the colorimetric study on gemology of jadeite and other gemstones [1-8], the equilibrium thermodynamic intelligent simulated calculation [9] is the main content of the theoretical study of rock formation. Most of the rocks in nature are formed in the period of a long-term geological history, but the experimental conditions on the formation of rocks cannot meet the time effect. Moreover, to the natural rocks for complex systems with multiple components, it is difficult to

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obtain the temperature-pressure condition and phase relation of the single variable line with defining significance for the mineral assemblage and its stable domain. The research method petrogenetic thermodynamics intelligent simulation has the advantages of without being limited by the experimental conditions, and it is benefit to get more information of rock formation with such large data simulation, such as any mineral-composition and mineral-content under temperature-pressure conditions, *etc.* The foundation of rock forming minerals' thermodynamic database and the intelligent computer numerical simulation technology is widely used, and that makes the method of rock formation of thermodynamics intelligent calculation based on end-members activity calculation unprecedented applicate [10, 11]. These theoretical calculation results are very close to the experimental results and the actual situation. The establishment of phase-relationship of jadeite is the important basis of both the explanation of relation between mineral composition and structure and acquisition of diagenetic conditions and evolutionary trends. The thermodynamic database of Powell [12-20] will be used to conduct a simulation study on the phase relationship of jadeite formation.

Rock thermodynamic model

When the metamorphism is balanced, it always shows $\Delta G_r^0 = -RT\ln K_{eq}$, where ΔG_r^0 is the difference of free energy of the standard state $K_{eq} = \Pi_{i=1}^{m} (a_i^{vi})$ – the equilibrium constant, R – the gas constant, a_i – the activity of constituent i, $a_i = X$, γ_i, X_i – the molar fraction of i, γ_i – the activity quotient, v_i – the reaction coefficient, m – the number of constituent. A solid solution mineral that is widely found in rocks, has two different models as ideal solution $\gamma_i = 1$ and non-ideal solution $\gamma_i \neq 1$, and after a series of derivations, the model expression of the symmetric normal solution of complex component system is obtained [5, 21]:

$$RT\ln\gamma i = -\sum_{k}\sum_{j>k}(X_k^0 - X_k)(X_j^0 - X_j)W_{kj} \tag{1}$$

Additi X_k^0 is the molar fraction of pure phase component k, $X_k^0 = 1$ when $k = 1$, otherwise $X_k^0 = 0$; X_k – the molar fraction of the composition of the actual mineral, W_{kj} – is the interaction energy between k and j, and it has nothing with mineral composition, but it might related to temperature and pressure, so its expression is $W_{kj} = a + bT + cP$ shows that when it has nothing with temperature and pressure $c = 0$, $b = 0$.

Tabela 1. The W_{kj} walue of end-members of jadeite

	Jd	Acm	Di	Hed
Jd	–	0	24	24
Acm	–	–	24	24
Di	–	–	–	3
Hed	–	–	–	–

Table 2. Activities of four end-members of jadeite

	Ideal condition (a^{Id})	Non-ideal condition (a)
Jadeite	$X_{Na}^{M2} \times X_{Al}^{M1}$	$\gamma_i \times a_{Jd}^{Id} = \gamma_i \times X_{Na}^{M2} \times X_{Al}^{M1}$
Augite	$X_{Na}^{M2} \times X_{Fe^{3+}}^{M1}$	$\gamma_i \times a_{Acm}^{Id} = \gamma_i \times X_{Na}^{M2} \times X_{Fe^{3+}}^{M1}$
Diopside	$X_{Ca}^{M2} \times X_{Mg}^{M1}$	$\gamma_i \times a_{Di}^{Id} = \gamma_i \times X_{Ca}^{M2} \times X_{Mg}^{M1}$
Hedenbergite	$X_{Ca}^{M2} \times X_{Fe}^{M1}$	$\gamma_i \times a_{Hed}^{Id} = \gamma_i \times X_{Ca}^{M2} \times X_{Fe}^{M1}$

Based on thermodynamic database from Holland [12, 13], the W_{kj} value of four end-members of Jd-Acm-Di-Hed were calculated, which shown in tab. 1.

The activity calculation model relates to the number of moles in the position of the mineral crystal, which can be obtained by analyzing the data of the mineral electron probe.

In the case of the previous four end-member minerals of jadeite, their activities in the ideal state and in the non-ideal state, as shown in tab. 2.

Thus, eq. (1) can be concretely reduced to the following:

$$\begin{aligned} \mathrm{R}T\ln\gamma_{\mathrm{Jd}} = -[&(1-X_{\mathrm{Jd}})(0-X_{\mathrm{Acm}})\times W_{\mathrm{Jd\text{-}Acm}} + (1-X_{\mathrm{Jd}})(0-X_{\mathrm{Di}})\times W_{\mathrm{Jd\text{-}Di}} + \\ &+(1-X_{\mathrm{Jd}})(0-X_{\mathrm{Hed}})\times W_{\mathrm{Acm\text{-}Di}} + (0-X_{\mathrm{Acm}})(0-X_{\mathrm{Di}})\times W_{\mathrm{Acm\text{-}Di}} + \\ &+(0-X_{\mathrm{Acm}})(0-X_{\mathrm{Hed}})\times W_{\mathrm{Acm\text{-}Hed}} + (0-X_{\mathrm{Di}})(0-X_{\mathrm{Hed}})\times W_{\mathrm{Di\text{-}Hed}}] \end{aligned} \tag{2}$$

After the transformation calculation is made by eq. (2), the mineral activity under certain temperature and pressure can be obtained.

Results

Jadeite can be simplified to be completed in the system of Na_2O-CaO-FeO-MgO--Al_2O_3-SiO_4-H_2O, and it can be abbreviated as the system of NCFMASH.

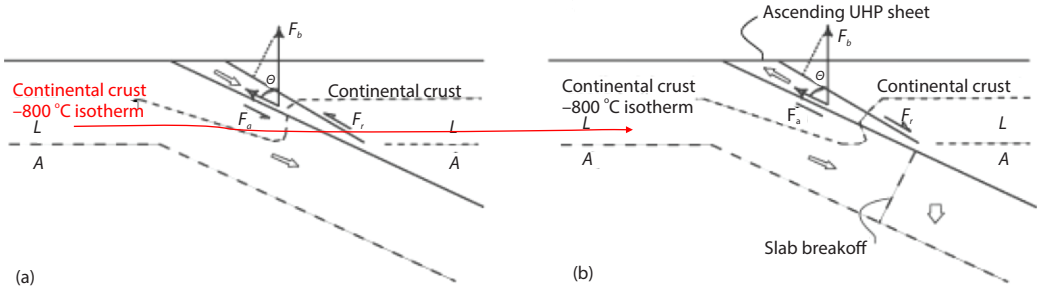

Figure 1. Diagenetic process of jadeite; *L, A – glide level, Fb – vertical upward stress, Fr – subduction stress, Fs – Subduction upward stress*

The two main methods of the mineral assemblage used in this system are the ideal combination of jadeite, albite, and quartz and the complex combination of jadeite, diopside, hedenbergite, kyanite and ferrotremolite. Different mineral assemblages reflect the different temperature-pressure conditions from different equilibrium.

Based on the electric probe of microanalysis (EPMA) data of the sample, and on the basis of thermodynamic calculation of the activity of each of its components, the temperature-pressure equilibrium thermodynamic calculation of each component of jadeite was conducted [22-24]. In order to make the data more reasonable, the calculation starts from 500 °C with an increases by 10 °C as a step and starts at 300 kb with an increases by 10 kb as a step.

Table 3. Chemical components of jadeite-jade

Sample	X-1-1	Gy-1	X-1-2	Bsj-2-B
SiO_2	57.61	56.26	58.75	50.60
TiO_2	0.07	0.06	0.20	0.40
Al_2O_3	12.57	5.55	1.98	9.38
Cr_2O_3	0.00	0.00	0.03	0.04
Fe_2O_3	0.00	0.00	0.00	0.00
FeO	1.59	2.99	2.75	3.42
MnO	0.02	0.28	0.12	0.11
MgO	7.42	20.35	19.69	17.56
CaO	10.13	7.84	2.722	7.51
CoO	0.11	0.00	0.06	0.37
NiO	0.04	0.05	0.00	0.00
K_2O	0.10	0.22	0.62	0.56
Na_2O	8.77	6.37	9.06	4.48
P_2O_5	0.38	0.03	0.22	0.99
Total	98.72	100.00	96.20	95.42

The temperature and pressure calculation of jadeite-jade in the system of Jd-Ab-Q

With the combination of Jd-Ab-Q (with some Kyanite) of sample X-1-2, the reaction is calculated:

– Ab → Jd + Q, the reaction of end-member mineral is albite and the stability coefficient is 0.0265
– Pa → Jd + Ky + H_2O, the reaction of end-member mineral is paragonite and the stability coefficient is –0.0123
– Q + Pa → Ky + Ab + H_2O, the reaction of end-member mineral is quartz and the stability coefficient is 0.102

The calculated equilibrium temperature is 751 °C and the equilibrium pressure is 17.0 kb.

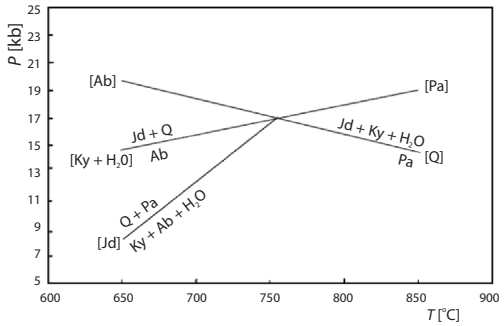

Figure 2. The P-T phase diagram of NCFMASH of jadeite, Sample X-1-2

The equilibrium temperature-pressure of this reaction is in agreement of that of the system $NaAlSi_3O_8$-$NaAlSiO_4$-SiO_2-H_2O, as shown in fig. 2, and is very closed to the equilibrium temperature-pressure of Jd-Ab-Q. It is testified that jadeite is stable when within the limits of under 800 °C and 21.70 kb, but it could formed the way as Jd + Ky + H_2O when the range is above the limits.

The pyroxene minerals are required to undergo ductile deformation at temperatures greater than 350 °C with 10.0 kb, and it is further explained that the toughness deformation of jadeite is not at least on the surface or near surface.

Jadeite has a similar crystal structure with other monoclinal pyroxene [25-27], where Si-O tetrahedron is formed by bridging oxygen to form a single chain silicate structure [28]. When subjected to external forces, the Si-O tetrahedral chain is not easy to break, but the bond angle of Si-O-Si is likely to change, and the slip of the chains is often formed the characteristic of monocline [001] (100) slip system. Due to the existence of the single slip plane in the crystal [29-31], when the jadeite crystal is subjected to external forces, especially when the crystal subjects the external force of the parallel sliding plane, the flexing and bending of the slip plane could occur. The average density $2 \cdot 10^9$-$2 \cdot 10^9$ Line/cm^2, for the reason of a slightly twisted dislocation of a jadeite crystal deformation.

Fibrous jadeite crystal shows clear twist shape distortions, obviously this is a strong clockwise torque result along [001] of jadeite crystal (looking down from the top). Plastic deformation under high temperature is illustrated by the residual deformation, because the strong bond force of Si-O in the jadeite single chain which connected by covalent bond, it is hard to be break, and so the crystal will ductility distorted only instead of fractured.

Jadeite crystal surface appears obvious irregular serrated trace. The obvious irregular serrated trace on the surface of jadeite crystal, divide jadeite into several smaller crystal continuously, which is the manifestation mode of ductile deformation inside jadeite crystal. The intracrystalline climbing of dislocation which formed by distortion, finally formed the dislocation wall locally with high dislocation density, and then formed the boundary of subgrain with the development of dislocation wall.

The temperature and pressure calculation of jadeite-jade in the system of Jd-Di-Hed-Ky-Fact-Ts-Cz

With the mineral association of Jd-Di-Hed-Ky-Fact-Ts-Cz in sample Bsj-2, the reaction is calculated as (in the brackets are the missing minerals in the system reaction):

– 4Ts + 5Q + 2Cz → 12Di + 11Ky + 5H_2O , [Fact, Hed], the stability coefficient is –0.00180

– 4Fact + 6Cz → 20Hed + Q + 9Ky + 7H_2O, [Ts, Di], the stability coefficient is –0.0854
– 5Fact + 21 Di + 8 Ky + 4Cz → 7Ts + 25Hed + 10Q , [H_2O], the stability coefficient is 0.0486
– 3Ts + 5Hed + 4Q → Fact + 9Di + 6Ky + 2H_2O, [Cz], the stability coefficient is 0.0160
– 11Fact + 27Di + 12Cz → 9Ts + 55Hed + 14Q + 8H_2O, [Ky], the stability coefficient is 0.149
– 5Fact + Ts + 12Cz → 3Di + 25Hed + 14Ky +10H_2O , [Q], the stability coefficient is –0.0624

In this system, the calculated equilibrium temperature of is 631°C and the equilibrium pressure is 18.8 kb.

The temperature and pressure range in the system of NCFMASH

In the NCFMASH system, with the reaction-line of two kinds of mineral composition meet at one point in fig. 3, the rock of jadeite could formed steadily under the rigorous environment of the fixed temperature-pressure. In fact, the formation of jadeite is accomplished in a range of variation of temperature-pressure range.

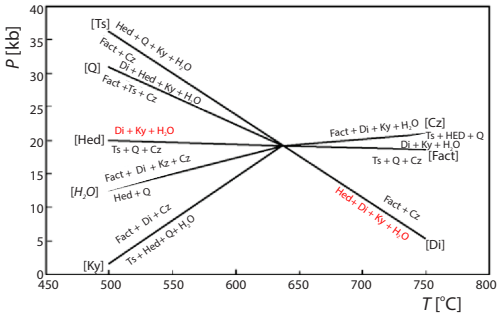

Figure 3. The P-T phase diagram of NCFMASH of jadeite, Sample Bsj-2

The following four reactions could be found in the process of the calculation of different temperature and pressure conditions:

– 6Parg + 22Q = Tr + 3Gl + 10Di + 6Ky + 2H_2O (P = 17.2 kb)
– Pa = Jd + Ky + H_2O (P = 17.6 kb)
– 2Fact + 12Di + 2Pa + 4Ky + Gl + 10Hed + 4Q (P = 18.0 kb)
– Tr + 2Pa = Gl + 2Di + 2Ky + 2H_2O (P = 18.8 kb)

Under the equilibrium pressure of 17.2 kb, 17.6 kb, 18.0 kb, and 18.8 kb, a closed temperature-pressure reaction section can be formed, as shown in fig. 4. This shows that in a small amount of sodium-mica (Pa), the balance of the system temperature should be between 700-700 °C, and balanced pressure range should be between 17.34-18.83 kb, which reflects the real balance temperature-pressure range of pure jadeite formation in the NCFMASH system.

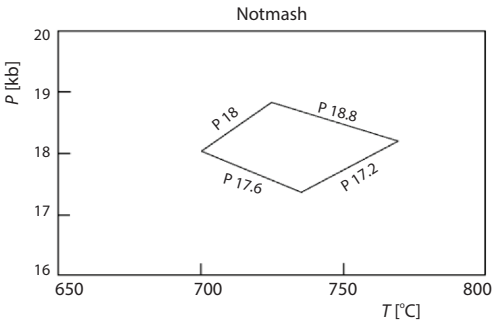

Figure 4. Closed reaction area of NCTNASH system

Conclusion

- In NCFMASH system, the results of the calculation based on the end-element activity show that the different mineral assemblages of jadeite reveals different temperature-pressure conditions during the formation of jadeite. The equilibrium temperature of the mineral assemblage of the hard jade sodium feldspar quartz is 751°C and the equilibrium pressure is 17.0 kb. The equilibrium temperature of the mineral assemblages of jadeite, calcium and ferrolite is 631°C, and the equilibrium pressure is 18.8 kb.
- With a small amount of sodium-mica, the results of the phase equilibrium intelligent calculation show that the jadeite in NCFMASH system will be formed in a closed temperature-pressure range within 700-770 °C and 17.34-18.83 kb.

- Through the calculation of phase equilibrium thermodynamic intelligence, a stable growth equilibrium temperature-pressure range of pure jadeite has been established to verify its metamorphism.
- Certain temperature-pressure is the necessary condition of high-quality synthetic jadeite, but the nature jadeite as a mineral aggregate undergoes dynamic metamorphism once or several times after its rock forming, it is unreasonable that jadeite synthesize is not just from one mineral crystals, and it is why the synthetic jadeite has yet to reach the gem quality.

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