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MICROSTRUCTURE AND ALKALI REACTIVITY OF SILICEOUS AGGREGATE

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ABSTRACT

By means of optic microscope, DSC and positron annihilation, the microstructures of various kinds of sand graves containing cryptocrystallites and different forms of chalcedony were studied in more detail. The results of observation under polarization microscope showed that from opal to quartz there are varieties of chalcedony. Their alkali reactivities are quite different according to their different microstructures. The classical examples of microstructures illustrated in this paper may help to distingush the degree of reactivity of aggregate. At the same time, from the datum obtained by DSC and positron annihilation could reflect the variety of cryptocrystalline quartz, which can be used to determine the alkali reactivity of quartz aggregate. These methods would be more meanigful than measurement of angle of undulatory extinction to investigate the disorder and alakli reactivity of strained or cryptocrystalline quartz.

1. INTRODUCTION

Most cases of deterioration of alkali-aggregate reaction were caused by siliceous aggregate, among them, the alkali reactivity of opal and chalcedony is the highest. As every one knows that macrocrystalline quartz is non-reactive. However, between them it is difficult to accurately determine the alkali reactivity of cryptocrystalline orstrained quartz. For example, Dolar-Mantuani[1] discovered that strained quartz is reactive as the angle of undulatory extinction[UE) bigger than 15^{o}, but Grattan-Bellew[2] concluded that no definite evidence of correlation between high UE angles in quartz in granitic rocks and the expansion of concrete contained them was found. Furthermore, the complexity of this problem is that there are many types of undulatory extinction, such as curve banding, twist-banding, broomed, lace-like, ring-like, massive, herring-bone, X-type and T-type extinctions. Among them, except banding extinction, it is difficult to determine the angle of UE for the other types of extinction. Moreover, the angle of UE could not be determined as the size of microcrystallite smaller than 2 µm. Thus, the alkali reactivity of quartz could be hardly determined by angle of UE, especially for microcrystalline quartz. It needs to explore new techniques to evaluate the defects of crystals of quartz. Thus, by using optic microscope, DSC(differencial scanning calorimeter) and positron annihilation, the microstructures and submicrostructures of quartz sands were studied by us in more detail from opal to quartz. The experimental results were described in this paper.

2. MICROSTRUCTURES

During the very long geological period, the metastable opal or chalcedony will gradually transform into well crystalline quartz. It can be expected that the alkali reactivity of siliceous aggregate will be reduced with the increasing degree of transformation. In order to prove this by experiments, thin sections of fifty samples contained various morphologies of chalcedony were prepared and observed through optic micrscope. The corresponding samples were examined by rapid test method suggested by us[3] to determine the values of expansion. A few experimental results were illustrated in Table 1 and Fig.1. It showed that there was close correlation between microstructures and alkali reactivities.

Table 1 Microstructures and Alkali Reactivities

No.	Minerals	Characteristics of Microstructures	Expansion (%)
1	Opal	Growth of fibre in cracks	1.324
2	Chalcedony	Classical chalcedony	0.497
3	Chalcedony	Fibre growing up	0.310
4	Chalcedony + quartz	Plumose fibre, partial fibre growing up to crystal	0.275
5	Chalcedony + quartz	Fibre growing up to coarse crystal	0.155
6	Quartz	Perfect crystal of quartz	0.043

* Note: >0.10% Reactive[3].

Table 1 and Fig.1 show that the alkali reactivity of opal is the highest in which the fibres of chalcedony grow in cracks(Fig.1, 1). Fig.1, 2 shows the classical radiating chacedony, its alkali reactivity is also very high. However, the alkali reactivity will be gradually reduced along with the growth of crystal, finally, it becomes non-reactive(Fig.1, 3-6). As a result, from the microstructures of petrographic analysis the degree of alkali reactivity can be roughly estimated. It is very helpful to determine the alkali reactivity as many photographes will be collected. For example, the alkali reactivity of Ottawa sand(provided by P.E. Grattan-Bellew) was not remarkable, even though it contained a few chalcedony, because the content was very low and the fibres of chalcedony have grown near perfect crystals of quartz(like Fig.1, 5). The value of expansion of this sand examined by rapid autoclave test method was 0.067%.

3. POSITRON ANNIHILATION TECHNIQUE

In the measurement of positron annihilation, the lifetime of capture positron(t_2, picosecond—ps) represents the length of defect. The intensity of capture annihilation(I_2 %) represents the intensity of long living component, that is the concentration of defect. So far, the defects of solid will increase as the values of t_2 and I_2 increasing. The datum obtained by this technique from more than fifty siliceous samples were treated by statistical method and the following equation wsa obtained:

$$P\ \% = 1.06\times10^{-3}(t_2 + 10I_2) - 0.524 \qquad (1)$$

P—Values of expansion obtained by rapid autoclave test method
t_2—Lifetime of capture positron annihilation, ps
I_2—Intensity of capture positron annihilation, %

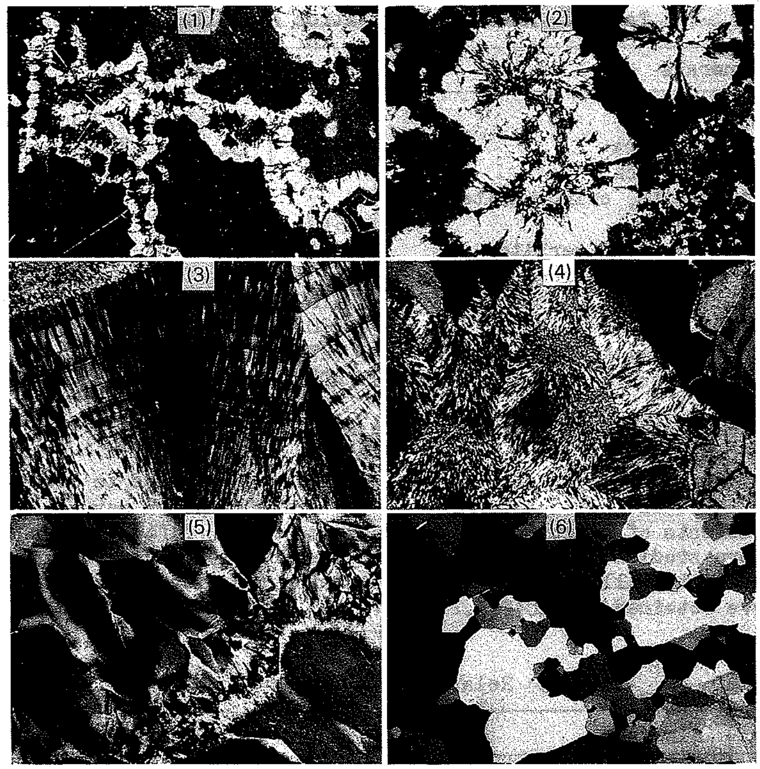

Fig.1 Mophologies from opal to quartz, (1) opal, (2),(3) chalcedony, (4),(5), Chalcedony + quartz, (6) quartz

Some of the experimental results are showed in Table 2. It is worth of note that the correlation of equation(1) is not very well. The coefficient of correlation of this equation is 0.824. Maybe there are another factors which influence the results. However, the statistical results gave following regularity: Let $R = t_2 + 10I_2$, then:

$R > 620$	Reactive
$620 > R \geq 550$	Potential reactive
$R < 550$	Non-reactive

4. EXPERIMENTAL RESULTS OF DSC

In the technical literatures of alkali-aggregate reaction, microcrystalline quartz were frequently described as reactive. But we discovered some flints being reactive, nevertheless, some other flints also containing microcrystalline quartz were non-reactive. Thus, it is difficult to distingush them by microscope. These samples examined by X-ray showed only characteristic dif-

Table 2 Results of Positron Annihilation

No.	Minerals	t_2(ps)	I_2(%)	R	P(%)
1	Opal	417	45.44	873	1.324
2	Fused silica	516	31.65	833	0.768
3	Silica brick (tridymite, cristobalite)	588	16.12	749	0.514
4	Chalcedony	549	26.93	818	0.497
5	Zeolitization perlite (containing chalcedony)	566	24.98	815	0.391
6	Chert(Guangxi, China)	416	31.94	735	0.200
7	Flint(Denmark)	420	30.46	725	Reactive*
8	Chert(Nanjing, China)	427	12.01	547	0.029
9	Quartz sand	408	9.04	498	0.020

*Note: proved by G.M. Idorn to be reactive.

fraction patterns of crystal of quartz. Therefore, we tried to study by means of DSC and expected that the temperature of transformation may be different for different defects of quartz crystals. Hence more than fifty samples of siliceous sand were studied by means of DSC. The experimental results showed that the alkali reactivity will increase with increasing the width of endothermic pick on the curve obtained by DSC(Fig.2, Table 3).

Table 3 Relationship between P and F

No.	Minerals	$F=lg[(T_2-T_1)/H]$	Expansion(%)
1	Quartz(sand)	0.397	0.020
2	Quartz(Yuhua stone, China)	0.446	0.043
3	Microcrystalline quartz	0.817	0.200
4	Microcrystalline quartz chalcedony	0.916	0.144
5	Chalcedony microcrystalline quartz	0.687	0.310
6	Chalcedony	1.047	0.497
7	Chalcedony microcrystalline quartz	1.269	0.200

The datum showed in Table 3 and Fig.2 were the partial results. From them it can be seen that between $\Delta T=T_2-T_1$ and the values of expansion of alkali reactivity obtained by rapid autoclave test method exists certain correlation. Respectively, T_1 and T_2(^oC) are the initial and final temperatures of transformation of quartz crystal near 573°C. In general, more larger ΔT, more smaller hight of pick(H, mW), the alkali reactivity is more remarkable, thus, let

$$F = lg[(T_2-T_1)/H] \quad (2)$$

$$P\% = a\ lg[(T_2-T_1)/H] + b = a\ lgF + b \quad (3)$$

where a and b are constants, P%, values of expansion of mortar bars treated by rapid autoclave test method. The coefficient of correlation of equation(3) obtained by statistical analysis of fifty samples is 0.649. It is not close corre-

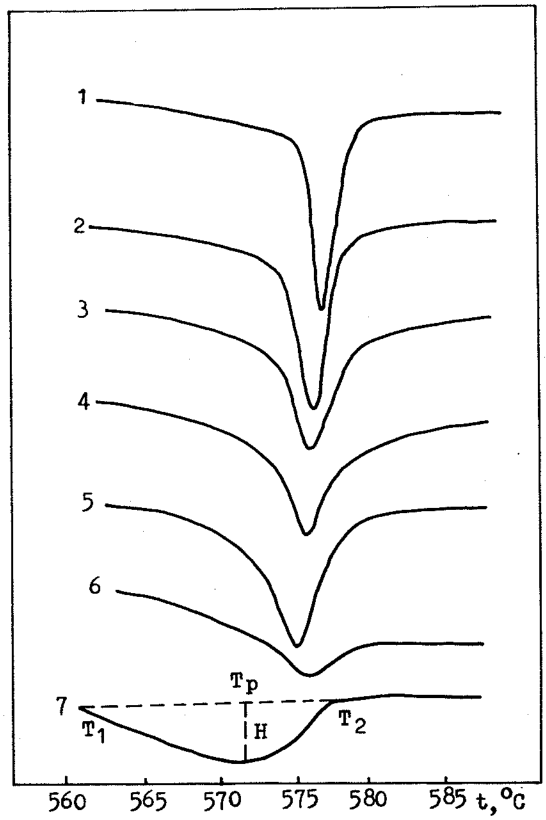

Fig.2 DSC, 1. quartz, 2. quartz, 3. microcrystalline quartz, 4. microcrystalline quartz and chalcedony, 5. chalcedony and microcrystalline quartz, 6. chalcedony, 7. chalcedony and microcrystalline quartz.

lation. However, according to the value of F we can distingush reactive from non-one:

F > 0.55	Reactive
F = 0.48-0.55	Potential reactive
F < 0.48	Non-reactive

This method can be also used to determine the alkali reactivity of few amount of quartz contained in rocks.

5. DISCUSSION

It is a very complex problem to determine the alkali reactivity of strained or cryptocrystalline quartz. We have tried to find out the relationship between porosity and alkali reactivity of quartz sand as suggested by some authors. But in our experimental results we have not discovered close correlation between them, the porosity was determined either by mercury porosimeter or by helium flow. The foregoing discussion illustrates that the positron annihilation technique and DSC are good techniques to evaluate alkali reactivity and seem worthy to further study. However, there are also some problems, for example, two flints, one from Denmark, the other from Nanjing, China, did not show any endothermic pick near 573°C, even though they showed obvious X-ray diffraction patterns of quartz, which made it difficult to use DSC to evaluate the alkali reactivity of quartz. In summary, in this respect the study was primary, further study is needed.

6. CONCLUSIONS

1. The microstructures from opal to chalcedony and quartz were studied in more detail. Collecting these characteristic photos would be very useful to determine the alkali reactivity of siliceous aggregate by optic microscope.

2. The positron annihilation technique can be used to evaluate the defects of quartz, and hence its alkali reactivity.

3. Samples of quartz with different defects of crystals showed different patterns in curve obtained by DSC. The width of endothermic pick will increase with the increasing defects of quartz crystals. So far, according to the data of wedening, the alkali reactivity can be evaluated.

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REFERENCES

[1] Dolar-Mantuani, L.M.M., Undulatory Extinction in Quartz Used for Identifying Potentially Reactive Rocks, Proceedings of Conference on Alkali-Aggregate Reaction in Concrete, Paper, No. S252/36, 6pp, National Building Research Institute of CSIR, Pretoria, S. Africa, 1981.

[2] Grattan-Bellew, P.E., Is High Undulatory Extinction in Quartz Indicative of Alkali-Expansivity of Granitic Aggregates? Proceedings of the 7th International Conference on Concrete Alkali-Aggregate Reactions, Noyes Publication, pp434-438, Ottawa, Canada, 1986.

[3] Tang Mingshu, Han Sufen and Zhen Shihua, A Rapid Method for Identification of Alkali Reactivity of Aggregate, Cement and Concrete Research, 13, 3, 417-422, 1983.