8th ICAAR 1989 KYOTO
8th Internationl Conference
on Alkali-Aggregate Reaction

DIAGENETIC CHANGES IN POTENTIAL ALKALI-AGGREGATE REACTIVITY OF SILICEOUS SEDIMENTARY ROCKS IN JAPAN —A GEOLOGICAL INTERPRETATION

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1. ABSTRACT

Petrographic studies were made of siliceous sedimentary rocks in Japan, including cherts, siliceous shales and their derivative metamorphics, together with related hydrothermally silicified rocks, based on microscopic observations, XRD analysis of silica minerals and the ASTM C289 chemical test. It was revealed that the potential reactivity of siliceous sedimentary rocks decreases drastically from Neogene diatomaceous rocks through late Mesozoic to Paleozoic radiolarian cherts during diagenesis and further metamorphism. This tendency is also recognizable in petrographic examinations, i.e. siliceous materials constituting these rocks tend to recrystallize through these geologic processes from an amorphous opaline state through an intermediate fine-grained mixture of chalcedony and microcrystalline quartz to a final coarse mosaic of granular quartz. This is paralleled by an increase in the crystallinity index as determined by XRD.

2. INTRODUCTION

There have been increasing reports on the occurence of alkali-aggregate reaction caused by siliceous sedimentary rocks in Japan (1,2). Similar rock types exist in US and the previous researchers have studied alkali-aggregate reaction without benefit of X-ray diffraction and other techniques (3,4). The present study relies on petrographic analysis using X-ray diffraction. A total of 60 specimens of cherts, siliceous shales, porcellanites, diatomites and flints, and their metamorphic counterparts such as chert hornfels and quartz schist, together with hydrothermally silicified rocks including petrified woods, agates and jaspers, were examined both by XRD and petrographically in conjunction with the ASTM C289 chemical test. Sample sourses range from Silurian to Miocene age. Reseach showing a distinct decrease in the reactivity of siliceous sedimentary rocks through diagenesis will be discussed in this paper.

3. GEOLOGICAL SETTING OF SILICEOUS SEDIMENTARY ROCKS IN JAPAN

Siliceous sedimentary rocks are widespread in Japan. Bedded cherts of Triassic age, among others, are extensively distributed in the Paleo-Mesozoic Chichibu Terrain, and most crushed stone used in concrete production comes from that terrain. Weakly metamorphosed siliceous shales and cherts also constitute local aggregate sources. On the other hand, opaline shales which resemble reactive Monterey Shale in California, are distributed in the Neogene Green Tuff regions, and river sands derived from them have caused alkali-aggregate reaction in this country (5). Most of hydrothermally silicified rocks, such as workable deposits of silicastone and local occurrence of agate and jasper formed though replacing rhyolitic tuffs, also belong to the Green Tuff regions.

4. ZONATION OF SILICEOUS SEDIMENTARY ROCKS

It is well known that opal, chalcedony and cryptocrystalline quartz, occurring in siliceous sedimentary rocks, are alkali-reactive (6). These minerals are essential constituents of cherts and siliceous shales whose origin is believed to be biogenic opal such as diatoms, radiolarians and siliceous sponges. Since opal is less stable, it would crystallize into stable quartz during long-term geologic processes as diagenesis or metamorphism. There is much field evidence for this assumption. For example, Murata et al.(7) reported that biogenic opal of Miocene diatomaceous Monterey Shale of California, is converted diagenetically into cryptocrystalline cristobalite (opal-CT) through progressive burial of the shale, which in turn is converted into microcrystalline quartz at a greater depth. Similar vertical distribution of the silica minerals is also recognized widely in Neogene profiles in Japan (8). Kinetic study of opal indicates that conversion of this mineral through cristobalite into quartz is promoted by the temperature and lapse of time, and that both opal and cristobalite should be transformed into stable quartz in pre-Tertiary rocks during burial diagenesis (9). Thus, diagenesis is the major factor controling the silica mineralogy of siliceous sedimentary rocks and is therefore definitely a key to assess the potential alkali-reactiivity of these rocks.

4.1 Diagenesis to Metamorphism

According to Iijima et al.(8), Neogene siliceous sedimentary rocks in Japan can be subdivided into the biogenic opal zone, the opal-CT zone and the quartz zone from top to bottom. They noted that opal-CT is transformed through chalcedonic to microcrystalline quartz in these rocks (10). In contrast, thick columns of pre-Miocene cherts in Japan, which are characterized by chalcedonic to microcrystalline quartz, have been lumped into the quartz zone (11). Because chalcedony has broad, five-fold peak patterns in XRD at a diffraction angle 67 to 69° in CuKa radiation (12), it is possible to distinguish this mineral from well-crystallized quartz by means of XRD. Murata et al.(13) defined the crystallinity index (CI) of quartz, based on the sharpness of this quintuplet, and showed that late Mesozoic cherts in California are better crystallized than Miocene cherts in the same region. They also noted that the CI value of quartz in the chert increases when metamorphism is superimposed on diagenesis. In our study, the following zonation, covering Miocene to Silurian siliceous sedimentary rocks, together with their metamorphic counterparts, has been adopted on the basis of petrographic study coupled with XRD measurement of CI values of quartz: the opal-A zone, the opal-CT zone, the chalcedonic/cryptocrystalline quartz zone, the microcrystalline quartz zone, and the granular quartz zone (Fig.1). The determination of CI is only meaningful when it is applied to the pure siliceous rocks like chert, because impure rock such as siliceous shale usually contains well-crystallized, clastic quartz that is not of diagenetic origin but raises the value.

4.2 Hydrothermal Silicification

Similar zonal distribution of the silica minerals has been noted in the aureoles of hydrothermal alteration, notably in the so-called silicification zone where the silica minerals occur, arranged in accordance with the increase in temperature toward the alteration center. Hayashi (14) reported that where the acidic hydrothermal solution has acted, opal and cristobalite characterize low temperature alteration, while quartz high temperature alteration. Local occurrence of hydrothermal opal, agate and jasper, as well as large workable silicastone deposits in Japan, are the product of this alteration.

5. PETROGRAPHIC CHANGES OF SILICEOUS SEDIMENTSRY ROCKS THROUGH DIAGENESIS

Siliceous sedimentary rocks of the Japanese Neogene are dominantly opaline and diatomaceous, while younger cherts from the upper Mesozoic to lower Miocene are chalcedonic, and older cherts from the Paleozoic to lower Mesozoic are largely quartzose and radiolarian. The CI value of the quartz in each rock was determined relative to the pegmatite quartz chosen for a standard as being 10.0 for its best crystallinity available. This value reflects the bulk crystallinity of quartz in the chert which contains a variety of quartz minerals of various crystallinty. However, a distinct increase in the crystallinity of quartz was noted from younger to older cherts. That is the CI increases from 3-5 in younger, chalcedonic to cryptocrystalline cherts, to 6-8 in older microcrystalline quartz cherts, and further to 9-10 in metamorphosed cherts (Fig. 1). A similar trend of increasing crystallinity of quartz was recognized in the course of alteration in the hydrothermally silicified rocks.

5.1 The Opal-A Zone

This zone is characterized by the presence of opal-A of biogenic origin, which is amorphous to XRD. The opal-A constitutes skeltons of siliceous fossils such as diatom frustules, radioralian tests and sponge spicules in the Miocene diatomites. This zone extends probably from Recent pelagic sediments down to late Miocene diatomaceous shales. Diatomites are only slightly indurated and not suitable for concrete aggregate.

5.2 The Opal-CT Zone

Siliceous sedimentary rocks of this zone are represented by moderately indurated siliceous shale and porcellanite, together with a hard opaline flint of biogenic origin. In these rocks poorly crystallized opal, which gives a broad XRD peak pattern of cristobalite with a shoulder of tridymite and thus called opal-CT, dominates. The zone occupies the middle Miocene strata. In this zone most of diatom skeltons dissolve in the rock while radiolarian tests and sponge spicules may persist. In some opaline flint chalcedonic quartz may appear within dissolved fossils, which is indicative of incipient crystallization of opal-CT into quartz mineral. Such transformation of opal is also found in a petrified wood of Miocene age. Hydrothermal opal characterized by opal-CT and cristobalite, can be correlated with this zone. Authigenic smectite commonly occurs as a pelitic impurity in this zone.

5.3 The Chalcedonic/Cryprocrystalline Quartz Zone (CI 3-5)

Younger cherts, since the late Mesozoic, are generally characterized by fine-grained, ill-defined matrix composed of chalcedonic to cryptocrystalline quartz. Such poorly crystallized chert ranges from early Miocene down to Jurassic, or sometimes Triassic age. In these rocks the grain size and optical orientation of each cluster of siliceous materials was not uniform, even in large size clusters. Clusters having such optical properties are approaching chalcedony. In some rocks, the entire matrix was composed of uniformly devided cryptocrystalline quartz, usually less than 5 microns across. Large fossils, like radiolarians and sponge spicules, are recrystallized into large chalcedony or microcrystalline quartz. The CI of the rock ranges mostly from 3-5. Authigenic illite or mixed-layer clay may be present.

On the other hand, a pure form of chalcedony occurs as agate mass in hydrothermally silicified rocks in the Miocene Green Tuff formations. Such typical chalcedony consists of fibrous quartz, of either parallel or radial arrangement, with wavy extinction. A sample section cut at right angles to the length of the fiber generally shows a cryptocrystalline texture of less than a few microns across. The CI value of the pure chalcedony averages 1-2. Jasper is a pigmented mixture of chalcedony and cryptocrystalline to microcrystalline quartz of hydrothermal origin, with the CI in the range of 3-5.

5.4 The Microcrystalline Quartz Zone (CI 6-8)

Older cherts of the early Mesozoic Trias and Paleozoic, are usually characterized by a coarser and complicated texture than that of younger cherts. The microscopic texture of the rock is not uniform, often having a bimodal distribution in the grain size of quartz. That is irregular-shaped mosaics or clusters composed of coarse-grained quartz with wavy extinction (20-40 microns), appear within fine-grained matrices composed of cryptocrystalline to microcrystalline quartz (up to 10 microns). SEM observations showed that the finer matrices of the chert are composed of discrete, polygonal shaped quartz. Frequent veins of coarse-grained quartz cutting through the rock also complicates the lithology. Thus the CI of the rock is high, attaining about 6-8. Radiolarias are the main fossils preserved, but subordinate amounts of sponge spicules may be recognizable. These fossils are selectively replaced by chalcedony or coarse mosaic quartz. Authigenic chlorite may be contained as an impurity of pelitic origin. Many hydrothermal silicastones resemble the chert of this zone in respect to the microscopic texture and crystallinity of quartz, except that the former have solution pores formed through hydrothermal leaching. The CI of the silicastones was 6-8.

5.5 The Granular Quartz Zone (CI 9-10)

In the aureoles of contact metamorphism or in the regional metamorphic belt, a distinctive grain growth of quartz takes place in the siliceous sedimentary rocks, which is promoted by an increase in temperature in these processes. Microcrystalline quartz in the chert recrystallizes into coarse-grained mosaics, composed of equigranular crystals with uniform extinction within each grain. Recrystallized cherts, such as chert hornfels and quartz schist characterized by a coarse texture, are the metamorphic counterparts of Paleo-Mesozoic sedimentary rocks described above. The grain size of quartz attains 20-50 microns in weakly metamorphosed hornfels, while it reaches 80-200 microns in intensely metamorphosed hornfels and quartz schist. The crystallinity of the quartz is high, with the CI attaining 9-10. In this zone pelitic impurity in the rocks crystallizes to biotite flakes.

6. INTERPRETING THE RESULTS OF THE QUICK CHEMICAL TEST

Results of the ASTM C289 chemical test indicate that a drastic change in the reactivity occurs in the course of diagenesis of siliceous sedimentary rocks, as a result of recrystallization of biogenic opal through chalcedony into quartz. The value of dissolved silica (Sc) and reductions in alkalinities (Rc) decreases from Miocene opaline shales, through late Mesozoic chalcedonic cherts, to early Mesozoic and Paleozoic quartzose cherts (Fig. 2). This change continues further into metamorphic quartzose cherts. Similar decrease in the reactivity from opaline through chalcedonic to quartzose rocks was also recognized in the hydrothermally silicified rocks mainly in the Green Tuff formations (Fig. 3). The effect of diagenesis that stabilizes reactive minerals through recrystallization, has been also noted on the post-Jurassic volcanic rocks in Japan (15). Measurements of the crystallinity index of quartz (CI) revealed a reverse correlation present between CI and the log of Sc, in both siliceous sedimentary rocks (Fig. 4) and hydrothermally silicified rocks (Fig. 5). This indicates that well-crystallized metamorphic quartz is less reactive than poorly crystallized quartz minerals, such as chalcedony and cryptocrystalline quartz. The measurment of CI, therefore, would give a rough estimate of the potential reactivity of pure siliceous sedimentary rocks.

6.1 Diagenesis to Metamorphism

Diatomites of the opal-A zone and opal CT zone showed the highest values of Sc and Rc among rocks tested (Sc 800 mmol/l, Rc>500 mmol/l). They fell into the potentially deleterious field (Fig. 2). The higher amounts of Sc are attributable to the large specific surface area of dominating diatom skeltons which consist of reactive opal (Fig. 4). Impure rocks such as diatomaceous shale, siliceous shale and porcellanite in these zones, in which opaline silica is diluted by terrigeous impurities, have a slightly lower Sc than that of diatomites. These rocks fell into the marginal innocuous field. An ASTM C227 mortar bar test of a marginal diatomaceous shale resulted in a moderate expansion (0.05% after one year, 1.20% eq. Na_2O) within a limit of the innocuous grade.

The value of Sc and Rc drastically decreases in the quartz zones (Fig. 2). Poorly crystallized younger cherts of the chalcedonic/cryptocrystalline quartz zone have lower Sc and Rc values (Sc 200-300 mmol/l) than those of opal zones. They range from potentially deleterious to deleterious. Moderately crystallized older cherts and siliceous shales of the microcrystalline quartz zone, resulted in even lower Sc values (Sc 80-150 mmol/l) than those of the former. They most frequently fell into the deleterious field as a result of a parallel decrease in Rc. Symptoms of the metamorphism were recognizable when the rocks have Sc less than 70 mmol/l. The most prominent effect of metamorphism is to recrystallize the quartz. This reduces the surface area of this mineral, thus alkali-reactivity is diminished. Strongly metamorphosed cherts and siliceous shales of the granular quartz zone, fell into the innocuous field with Sc less than 40 mmol/l, which is approaching well-crystallized pegmatite quartz (Sc 27, Rc 11).

6.2 Hydrothermal Silicification

Both hydrothermal opals and diagenetically silicified wood, containing cristobalite, have the highest value of Sc and Rc in the potentially deleterious field (Fig.3). Pure chalcedonies and most of the jaspers fell into the potentially deleterious field around Sc 700 mmol/l, Rc 200 mmol/l. On the other hand, hydrothermal silicastone, which is dominated by microcrystalline quartz, like the chert, fell generally into the deleterious field with Sc 60-120 mmol/l with small Rc values. Thus, the trend of reactivity of silicified rocks is very similar to that of diagenesis, despite the difference in origin that silica minerals in these rocks were crystallized from hydrothermal solutions.

7. CONCLUSIONS

Petrographic studies, coupled with measurements of the crystallinity index of quartz (CI) and ASTM C289 testing, revealed that potential reactivity of Japanese siliceous sedimentary rocks decreases drastically from Neogene opaline shales and diatomites (CI 0) through late Mesozoic chalcedonic cherts (CI 3-5), to early Mesozoic and Paleozoic microcrystalline quartz cherts (CI 6-8), and further to metamorphic quartz cherts (CI 9-10). This is the result of recrystallization of reactive biogenic opal through poorly crystallized chalcedonic quartz into coarse-grained, well-crystallized stable quartz during diagenesis and further metamorphism. Diagenesis is therefore a controling factor of the complex alkali-reactivity of siliceous sedimentary rocks. Similar mineralogical changes occur even within a short geologic period in hydrothermal silicification.

8. ACKNOWLEDGEMENT

The authors are grateful to Mr.Kazuo Naruse, chief chemist of the Utsunomiya Laboratory of the Sumitomo Cement Co.,Ltd., for his analysis of the quick chemical test.

REFERENCES

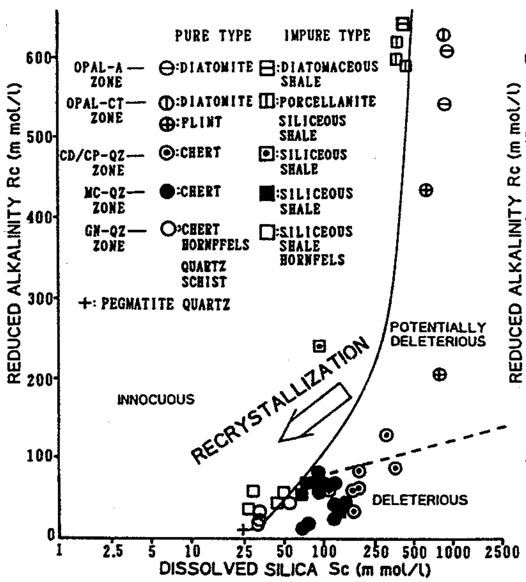
(1) Kusano,M.,Kobori,K.,Yamada,M. and Tazawa,E., Proceedings of the 7th JCI Conference, 125-128. 1985. (*)
(2) Morino,K., Journal of Japan Institute of Aggregate Technology, 18, 63-73.1986. (*)
(3) Stanton,T.E., Proceedings of the American Society of Civil Engineers, 66. 1781 -1811. 1940.
(4) Mather,B., Poceedings of the Highway Reseach Board, 31, 218-233. 1952.
(5) Kondo,Y. and Kitagawa,K., Semento Gijutsu Nenpo, 5, 379-399. 1951. (*)
(6) Mielenz,R.C., ASTM Proceedings, 54, 1188-1218, 1954.
(7) Murata,K.J.and Larson,R.R.,U.S.Geological Survey Journal, Research, 3, 553-566.1975.
(8) Iijima,A. and Tada,R., Sedimentology, 28, 185-200, 1981.
(9) Mizutani, Sedimentology, 15, 419-436, 1970.
(10)Tada,R. and Iijima,A., in Siliceous Deposits in the Pacific Region, 229-245, ed.Iijima,A., Hein, J.R. and Siever,R. Elsevier, 1983.
(11)Kakuwa,Y., Scientific Papers of the College of Arts and Sciences,the University of Tokyo, 34, 43-61, 1984.
(12)Iwai,S., Ossaka,J. and Morikawa,H., Yogyo Kyokai Shi, 77, 172-178, 1969.
(13)Murata,K.J. and Norman,M.B., American Journal of Science, 276, 1120-1130, 1976.
(14)Hayashi,M., Journal of the Japan Geothermal Energy Association, 10, 9-46, 1973.
(15)Katayama,T. and Kaneshige,Y., Proceedings of the 7th International Conference of Alkali-Aggregate Reaction in Concrete, Ottawa, 1986. 489-495. (publ.1987)

(*) in Japanese

ZONE \ AGE	CENOZOIC: MIOCENE	CENOZOIC: PRE-MIO	MESOZOIC: CRETA.	MESOZOIC: JURA	MESOZOIC: TRIAS	PALEOZOIC: PERM.	PALEOZOIC: CARB.	PALEOZOIC: DEV.	PALEOZOIC: SIL.	QUARTZ: C. I.	QUARTZ: GRAIN SIZE
OPAL-A ZONE	—										
OPAL-CT ZONE	—										
CHALCEDONY *	—									1−2	< 2-5μ
CHALCEDONIC/ CRYPTOCRYSTALLINE QUARTZ ZONE	—	( )	—	—	--					3−5	< 2-5μ
MICROCRYSTALLINE QUARTZ ZONE				--	—	—	—	( )	—	6−8	<10μ 20-40μ
GRANULAR QUARTZ ZONE			--	--	-- METAMORPHISM	--				9−10	>20-50μ

* HYDROTHERMAL PRODUCTS IN THE GREEN TUFF REGIONS

FIG. 1 DISTRIBUTION OF SILICA MINERALS IN THE SILICEOUS SEDIMENTARY ROCKS IN JAPAN



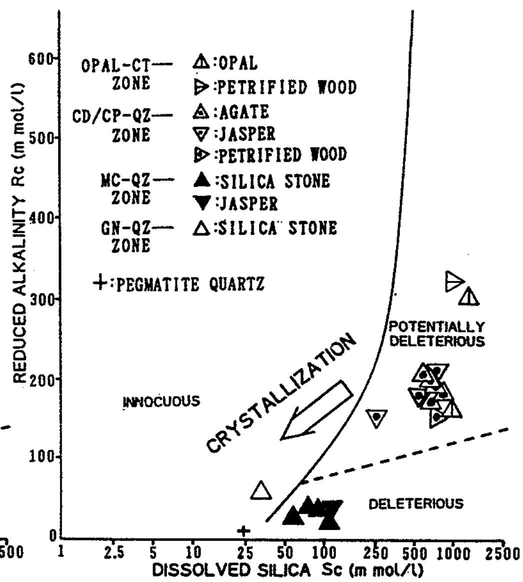
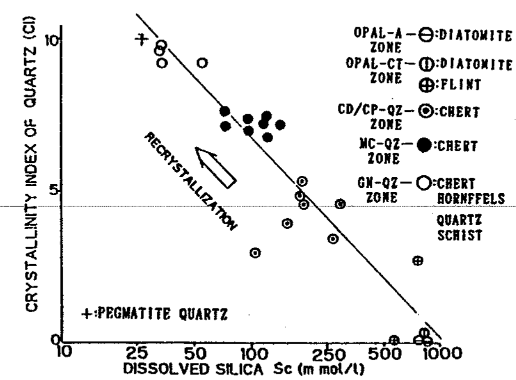


FIG. 2 ASTM C289 TEST OF SILICEOUS SEDIMENTARY ROCKS IN JAPAN

FIG. 3 ASTM C289 TEST OF HYDROTHERMALLY SILICIFIED ROCKS IN JAPAN



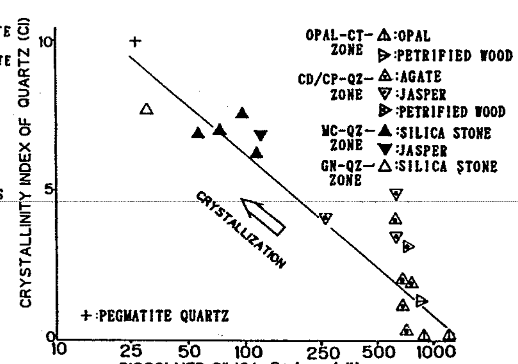


FIG. 4 PLOTS OF SC AGAINST CI OF SILICEOUS SEDIMENTARY ROCKS

FIG. 5 PLOTS OF SC AGAINST CI OF HYDROTHERMALLY SILICIFIED ROCKS