MINERALOGICAL INTERPRETATIONS OF DISSOLVED SILICA
AND REDUCTION IN ALKALINITY OF THE CHEMICAL METHOD

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Abstract:The chemical method (JIS A 5308) and mineralogical experiments have
been carried out on main rock forming minerals and rocks. The results indicate
that dissolved silica (Sc) of the minerals are fixed by their silica content,
thermodynamic instability, amount of non-bridging oxygen, crystallinity and
grain size, and reduction in alkalinity (Rc) by presence of expanding clay min-
erals and grain size. Thus, reactivity of rocks are roughly derived from mineral
assemblages and grain size of the rocks.

1. INTRODUCTION

Alkali reactivity of rocks is very complicated, because the rocks are com-
posed of many kinds of minerals and mineral assemblages of the rocks are quite
various by each rock. Then, to understand the alkali reactivity of the rocks,
we determined reactivity of main rock forming minerals and rocks by the chemical
method. Mineralogical investigations for the results of the chemical method
were performed. As the results, dissolved silica and reduction in alkalinity
could be interpreted mineralogically. An outline of this paper was previously
reported (1)(2).

2. ALKALI REACTIVITY OF MINERALS

2.1 Sc and Rc of minerals

Alkali reactivity of main rock forming minerals were determined by the
chemical method (JIS A 5308:modified method of ASTM C 289). The results of the
chemical method were represented by dissolved silica (Sc) and reduction in alka-
linity (Rc). By which values, reactivity of sample is divided into "innocuous",
"potentially deleterious" and "deleterious". In this paper, samples which are
plotted in the deleterious and potentially deleterious regions are considered
to have alkali reactivity.

Fig.1 shows distribution of Sc and Rc of the minerals. These minerals are
divided into two groups. One has the very low Rc and the wide range of Sc (group
A). The other has high Sc and Rc (group B).

2.2 Mineralogical factor to determine Sc

In group A, felsic minerals have higher Sc than mafic minerals. This sug-
gests that chemical composition determines Sc value. Sc is roughly correlated

with silica content of the minerals as shown in Fig.2. In these minerals, cristobalite, tridymite and mafic minerals do not indicate correlation. Silica content of cristobalite and tridymite are the same as that of quartz, nevertheless the Sc are much higher than the Sc of quartz. This very high Sc is attributed to their thermodynamic instability. The mafic minerals have the lowest Sc, but their silica content are higher than muscovite. The cause of their low Sc is attributed to their basicity. Mafic minerals .re weak base, because they contain MgO, CaO, etc.. And they are not easily dissolved by basic solutions such as NaOH.

Glasses also indicate high Sc in group A. High Sc values of glasses are related to their crystal structures. Glasses are composed of very irregular arrangements of SiO$_4$ frameworks. Thus, glasses have little bridging oxygen as compared with silicate minerals. To dissolve silica from materials, SiO$_4$ frameworks must be broken down at the bridging oxygen. Accordingly, glasses can easily release silica.

In natural glasses, the Sc of perlite (group B) is higher than that of obsidian. Diamond (3), Nagashima et al. (4) and Takinaga et al. (5) describe that perlite has large specific surface because it is porous, so that it has higher Sc than obsidian.

Cherts are mostly composed of quartz, but Sc of cherts is very high as compared with rock crystal (quartz). It is considered that crystallinity and grain size of quartz in the cherts cause this high Sc. Fig.3 shows the relationship between Sc and crystallinity of quartz in the cherts. The crystallinity is derived from the Murata and Norman's method (6) (not using the scaling factor in this paper). It is clear that the Sc correlates to the crystallinity. Probably, low crystallinity quartz has abundant non-bridging oxygen, thus, it dissolves easily in NaOH as well as the glasses. Gogte (7) mentions that rocks contain-
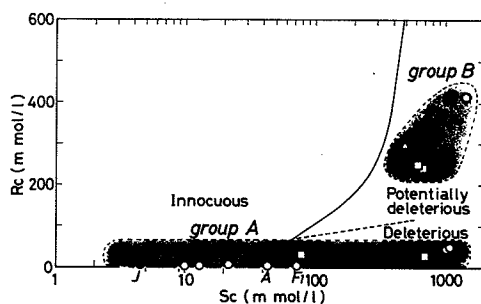

Fig.1 Plots of Sc *versus* Rc for the minerals. Boundaries were based on ASTM. Felsic min., A:quartz, B:cristobalite, C: tridymite, D:opal, E:K-feldspar, F1,2:plagioclase, G:muscovite, Mafic min., H:hornblende, I:enstatite, J:augite; Glasses, K:obsidian, L:pylex glass, M:perlite; Clay min., N:montmorillonite. Data of B, C are from Kusakabe *et al.* (9).
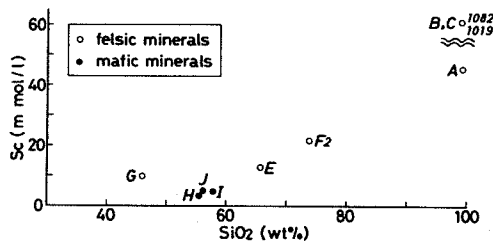

Fig.2 Correlation of SiO$_2$ *versus* SC for the minerals. SiO$_2$ content was analyzed by wet process. The symbols are the same as the Fig.1.
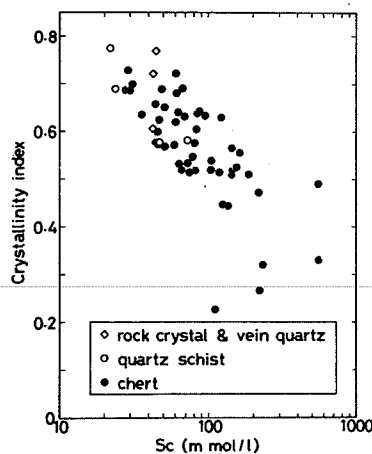

Fig.3 Correlation of Sc *versus* crystallinity for quartz.

ing strained quartz observed by optics are moder-
ately reactive.

Grain size of minerals is also related to
Sc. Fig.4 shows relationships between crushed
grain size and Sc. They have a good correlation.
When, grain size becomes small, specific surface
becomes large, the reaction may be accelerated.
Also for this reason, quartz in the cherts shows
high Sc (8)(9)(10)(11), (see Fig.6).

It is concluded that minerals which have
high Sc are high silica content and/or thermo-
dynamically unstable and/or abundant non-bridging
oxygen and/or low in crystallinity and/or small
in grain size. Cristobalite, tridymite, opal,
glasses and fine grained quartz provide these
conditions.

2.2 Mineralogical factors to determine Rc

All the minerals belonging to group B have
high Rc. Montmorillonite is one of the expanding
clay minerals, which performed ion exchange be-
tween alkali and alkaline earth ions in solutions
and its interlayer cation. When montmorillonite
is immersed in NaOH solution, Na may be absorbed
in montmorillonite. Nishizaki (12) reports that
Na content in a solution containing montmorillon-
ite-bearing rocks is lower than in the solution
without such rocks. This indicates that Na in
solutions is absorbed in montmorillonite. By this
ion exchange, montmorillonite shows high Rc (see
Fig.8).

Grain size of minerals is concerned with
Rc too. Their correlation is negative, as in the
case of Sc (Fig.5). Rc of perlite and opal are
high by their large specific surface. Probably,
montmorillonite-bearing rocks have large specific
surface and this is another cause of their high
Rc.

Fig.4 Relations between
Sc *versus* grain size
(2).

Fig.5 Relations between
Rc *versus* grain size
(2).

3. ALKALI REACTIVITY OF ROCKS

3.1 Mineral assemblages of rocks and their alkali reactivity

It is considered that Sc and Rc of rocks can be calculated from Sc, Rc
and grain size of constituent minerals. Calculated Sc and Rc are derived from
weighing the mean of Sc and Rc of constituent minerals (2). But this method
is applied only when Sc of constituent minerals are similar to each other. If
a high Sc mineral is contained in a rock, observed Sc is higher than calculated
Sc. However, Sc and Rc of rocks are provided from the mineral assemblages and
grain sizes of minerals.

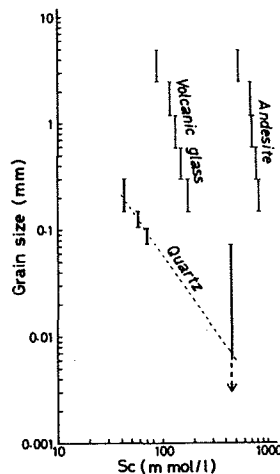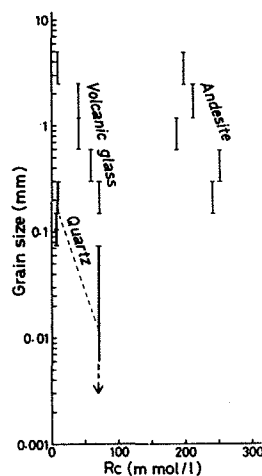### 3.2 Alkali reactivity of rocks

Fig.6 Plots of Sc *versus* Rc for the rocks.

Fig.7 Correlation of Sc *versus* cristobalite and /or tridymite content of the volcanic rocks. Content of the minerals were roughly determined by X-ray diffractometry.
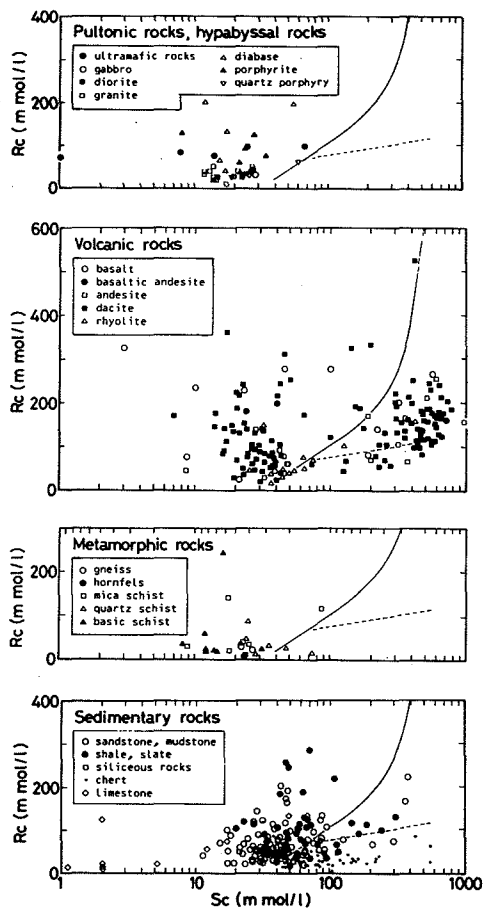
In this section, we discuss the relationships between alkali reactivity and mineral assemblages of the rocks by each rock type. Fig.6 shows plots of Sc and Rc by rock type.

Pultonic rocks do not have high Sc minerals, and their grain sizes are large. Thus, they are not reactive.

Parts of volcanic rocks contain cristobalite, tridymite, glasses and montmorillonite. Their Sc and Rc indicate various values. Mostly, Sc of cristobalite and/or tridymite and/or glasses containing rocks are higher than 100 m mol/l (Fig.7). If montmorillonite is born in rocks, Rc is higher than 150 m mol/l (Fig.8). If montmorillonite is not born in these rocks, Rc may be low.

Most metamorphic rocks do not have high Sc minerals. Hence, most rocks are not reactive. Two samples belonging to quartz schist have reactivity, because they are originally cherts.
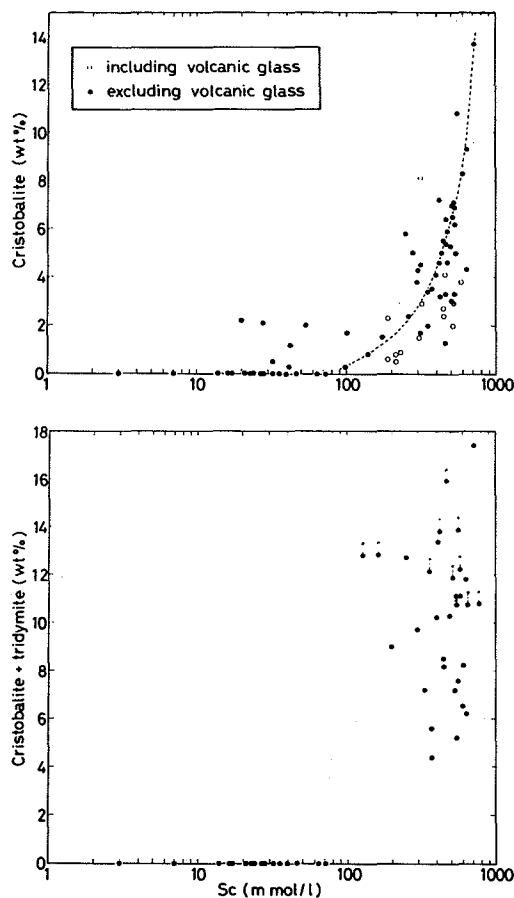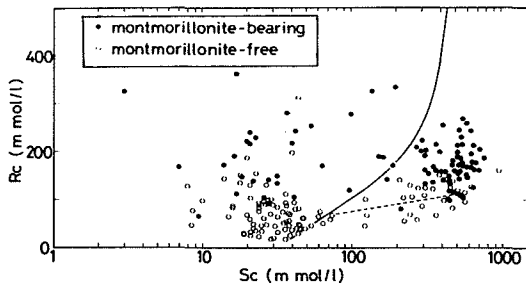
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Fig.8 Relationships Sc and Rc *versus* presence of montmorillonite in the volcanic rocks.
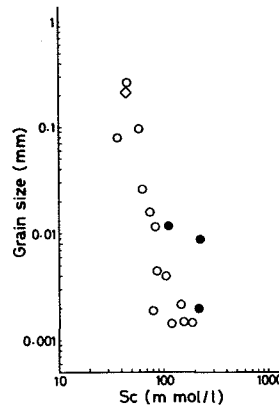

Fig.9 Correlation of Sc *versus* grain size for the cherts.

Sc and Rc of sedimentary rocks have a very wide range. In sedimentary rocks, most cherts are reactive, because quartz in cherts have low crystallinity (Fig.3) and fine grain size (Fig.9). Other reactive sedimentary rocks have chalcedony and quartz which is the same as in cherts.

3.3 Relationships between Sc, Rc and mortar bar expansion

As shown in Fig.10, the results of the chemical method (Sc, Rc) and expansion of mortar bar have good correlation by rock type. However, expansion of most rocks belonging to the potentially deleterious are over 0.1% per 6 months. This cause is mineralogically considered in that the Rc of the these rocks is apparently high, because they contain montmorillonite.
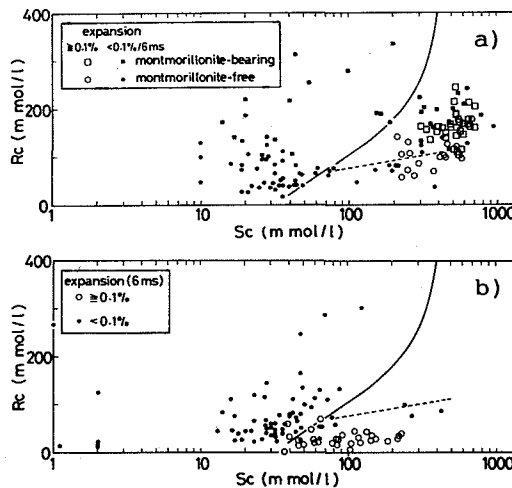

Fig.10 Diagrams showing relations between Sc and Rc *versus* mortar bar expansion. a) volcanic rocks, b) sedimentary rocks.

4.CONCLUSIONS

Sc and Rc of rock forming minerals are determined by mineralogical factors. High Sc is brought by high silica content, thermodynamic instability, a large amount of non-bridging oxygen, low crystallinity and small grain size (large specific surface). Crystobalite, tridymite, opal and glasses provide these conditions. Ion exchange properties of clay minerals and small grain sizes carry out high Rc. Reactivity of a rock is roughly known from its constituent mineral assemblages and grain size.

In volcanic rocks, Sc and Rc are determined by the presence of cristobalite, tridymite, glasses and montmorillonite (Fig.11a). Whereas in sedimentary rocks, reactivity is mainly fixed by crystallinity and grain size of quartz in rocks (Fig.11b).
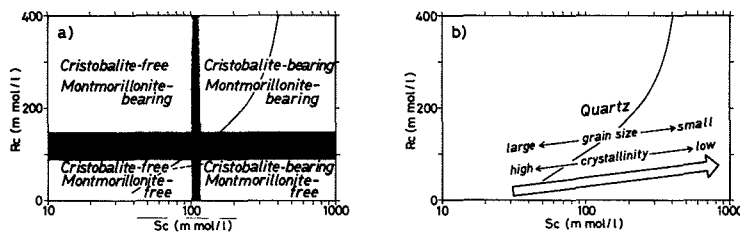
Fig.11 Correlations of Sc and Rc *versus* mineralogical conditions. a) Volcanic rocks. Ability to determine Sc of tridymite is the same as cristobalite. The shaded area is transitional zone. b) Sedimentary rocks.

Sc, Rc and expansion of mortar bar have a good correlation. Then, we can predict reactivity (Sc, Rc and mortar bar expansion) of rocks by mineralogical data of the rocks.

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*(J):in Japanese, **(JwE):in Japanese with English Abstract.