DISSOLUTION OF TWO AUSTRALIAN PALYGORSKITES IN DILUTE ACID

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Abstract—The dissolution of two relatively pure Australian palygorskites in mild acid was studied. For both palygorskites, Si and Mg releases were linear with respect to added acid. The rate of Si release with acid addition is equal to 0.66 μmol Si for each μmol H^+ added in both palygorskites. The corresponding releases of Mg were 1.2 μmol for the Al-poor and 0.47 μmol for the Al-rich minerals. Mg appears to be preferentially released into solution over Si, and both Mg and Fe appear to be preferentially released into solution over Al, suggesting a lower stability of Mg and Fe-rich palygorskites compared to Al-rich varieties. The free energy of formation of one of the palygorskites was estimated as equal to −1143.7 kcal/mol.

INTRODUCTION

Reports of the occurrence of palygorskite in soils and sediments have been proliferating in recent scientific literature. A variety of explanations for the mode of formation of this mineral has been offered (Isphording, 1973), yet little experimental work has been carried out to substantiate any of the theories of formation.

The main obstacle in the way of experimental work is the scarcity of monomineralic material. In most of the known palygorskite deposits, accessory minerals are present in varying amounts. When these accessory minerals include clay minerals, as is frequently the case, separation of pure palygorskite is, at present, extremely difficult. Analytical work with impure material, however, unavoidably introduces approximations which are difficult to assess.

Several studies have been devoted to the decomposition of palygorskite by strong acids (Nathan, 1968; Abdul-Latif and Weaver, 1969; Mendelovici, 1973). Important information on the structure of the mineral was obtained by these studies. However, the aggressive environment created by the strong acid can hardly serve as a model for the natural medium in which clay formation commonly takes place.

The aqueous dissolution of an Australian palygorskite has been studied in a previous paper (Singer and Norrish, 1974). In the present study, the dissolution of two palygorskites in very weak acid was examined.

EXPERIMENTAL

Materials

Both palygorskite minerals chosen for the present work occur in deposits from Australia. These deposits contain no admixtures of other clay minerals and were therefore considered to be well suited for experimental work. One is from Mt. Flinders, near Ipswich, Queensland, and has been described by Rogers *et al.*

(1954). The second is from Mt. Grainger, Southern Australia. It occurs in the form of mountain cork, in association with siliceous magnesian limestone, and probably has formed as a result of the decomposition of the limestone (Dep. of Mines Rep., 1919). Both contain appreciable amounts of calcite. In addition, the Mt. Grainger palygorskite contains considerable amounts of dithionite extractable iron. Apart from these accessory minerals, both palygorskites were remarkably free of other aluminosilicates.

The palygorskites were treated first with H-saturated Duolite CS-101 ion exchange resin, at a pH of >4. for the removal of carbonates. The materials were then Na saturated, dispersed and the < 2-μm fraction separated. To the Mt. Grainger palygorskite the dithionite citrate method was applied for the removal of the free iron oxides. The clays were then Ca-saturated. The chemical analysis of the purified minerals, carried out spectrographically with a high degree of accuracy, after Norrish and Hutton (1969), is given in Table 1. From these data, it can be seen that the palygorskites do not contain any elements indicating the presence of impurities. This is also evident from the relatively low exchange capacities. The two minerals differ considerably from each other. The Mt. Flinders clay is Mg- and Fe-rich and correspondingly low in Al. The Mt. Grainger palygorskite, on the other hand, is relatively high in Al, correspondingly lower in Mg and Fe. The chemical structure formulae calculated from the compositions are also given in Table 1.

Methods

For the acid dissolution experiment, 50 mg of the Ca-saturated clay was suspended in 25 ml of M/20 $CaCl_2$ solution to which the required amounts of dilute HCl, made up in the same salt, had been added. The final solutions had H^+ concentrations in the range from 5 to 100 μmol H^+/25 ml. The solutions

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Table 1. Chemical composition of 2 Australian palygorskites determined spectrographically after Norrish and Hutton (1969)* (ignited basis)

	Mt. Flinders	Mt. Grainger
SiO_2	70.473	73.340
Al_2O_3	6.844	14.071
Fe_2O_3	5.656	1.857
TiO_2	0.694	0.019
MnO	0.066	0.058
CaO	0.219	0.357
MgO	15.904	10.241
P_2O_5	0.038	0.035
K_2O	0.004	0.076
Total	99.900	100.05
Moisture loss	8.99	8.98
Ignition loss	13.18	13.87
Ex. cap.	6 mequiv./100 g	10 mequiv./100 g

* Mt. Flinders palygorskite analysis from Singer and Norrish (1974).

containing the clay were shaken in 50-ml polypropylene centrifuge tubes for time intervals ranging from 6 to 420 days, at 25°C ± 0.5. After shaking, the pH in the suspensions was measured, they were then centrifuged and aliquots taken for analysis. Concomitantly clay samples were also shaken with distilled water until dissolution increments with time became negligible. The pH was determined with a glass electrode in conjunction with a saturated calomel reference electrode, and Si, Mg, Al and Fe were determined by atomic absorption with a Perkin–Elmer, Model 303 apparatus.

RESULTS AND DISCUSSION

Figures 1–6 represent the net (release in water subtracted from total release) dissolution of Si and Mg for both palygorskites and that of Al and Fe for the
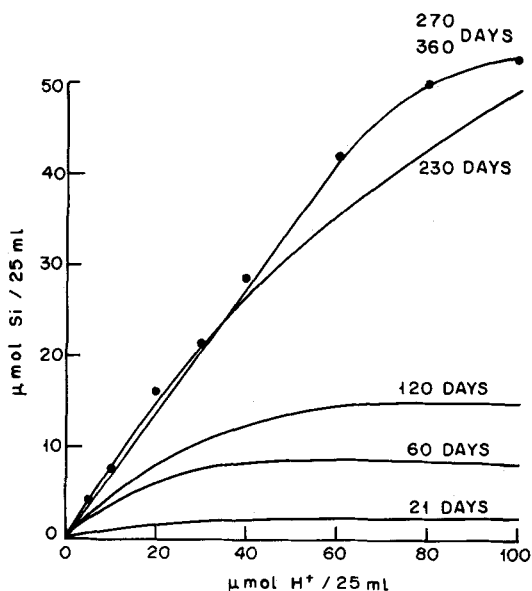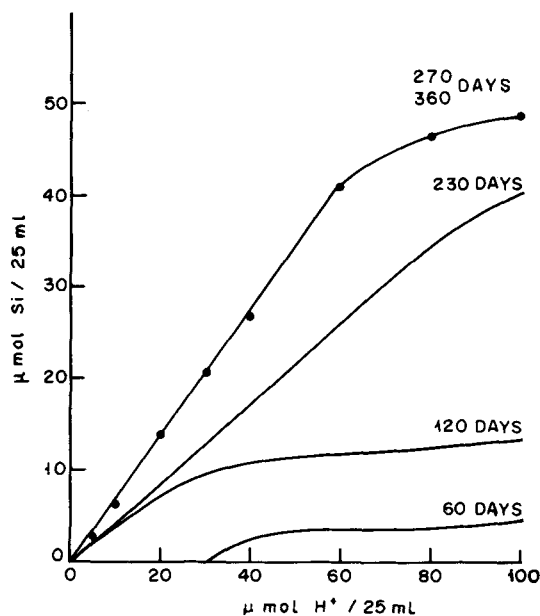
Figure 2. Net dissolution of Si from Mt. Grainger palygorskite after different reaction times with added acid.

Mt. Grainger palygorskite alone. Limiting pH values prevented the dissolution values of Al and Fe from the Mt. Flinders palygorskite from having any significance.

A considerable time was required to achieve equilibrium with respect to all constituents released. Equilibrium in the release of Si was achieved only after 270 days (Figures 1 and 2). The release of Mg, Al and Fe continued for much longer periods, of up to 360 days (Figures 3–6). Beyond 360 days there were no further significant increases in the amounts of dissolved constituents.

Figure 1. Net dissolution of Si from Mt. Flinders palygorskite after different reaction times with added acid.
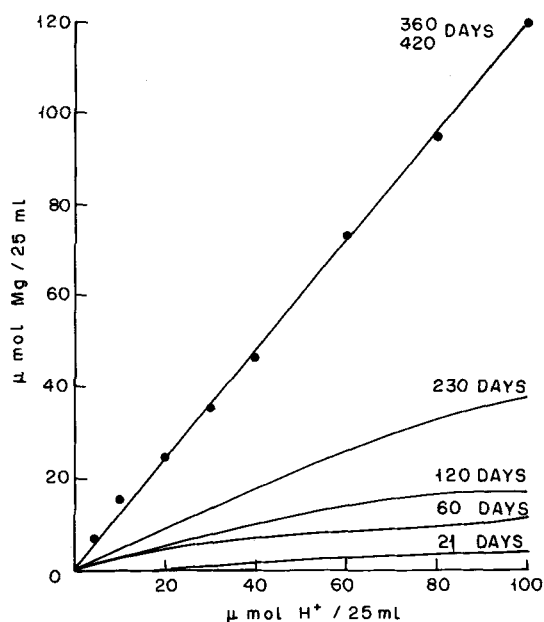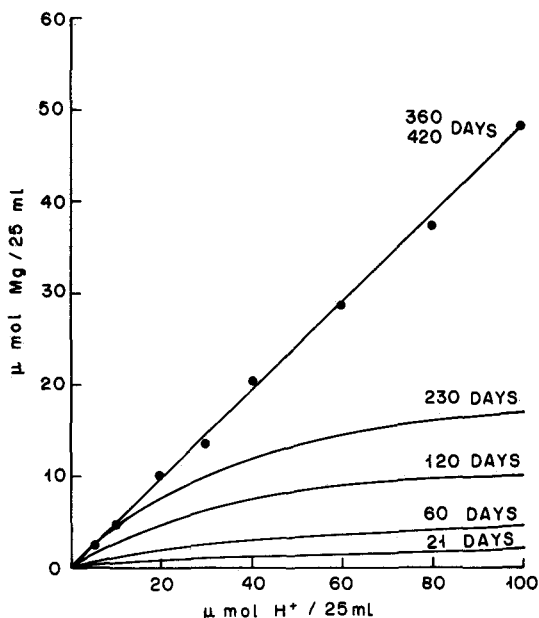
Figure 3. Net dissolution of Mg from Mt. Flinders palygorskite after different reaction times with added acid.
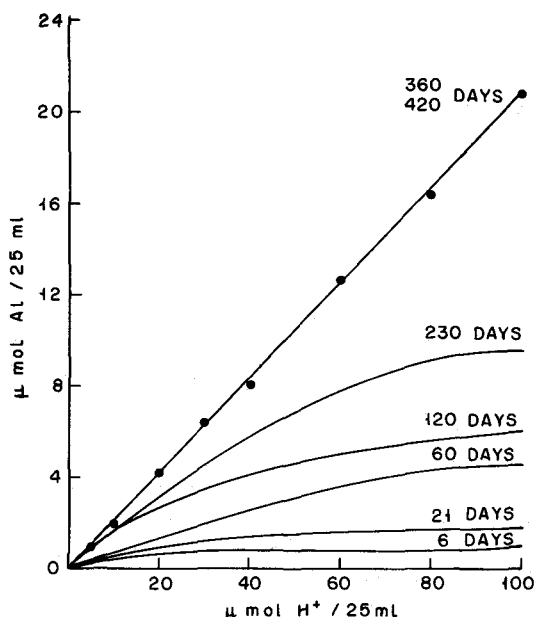
Figure 4. Net dissolution of Mg from Mt. Grainger paly-
gorskite after different reaction times with added acid.

Figure 6. Net dissolution of Fe from Mt. Grainger paly-
gorskite after different reaction times with added acid.

For most of the acid added, Si release is linear. As the solubility limits of amorphous silica (about 140 ppm or 50 μmol/25 ml) were approached at the higher added H^+ levels, the rate of silica release decreased. At the higher acid levels, release of Si was lower with Mt. Grainger palygorskite than with Mt. Flinders. This effect is attributed to suppression of Si solubility due to the greater availability of Al (Okamoto et al., 1957).

For both palygorskites the rate of Si release with acid addition appears to be similar and equal to 0.66 μmol Si for each μmol H^+ added. Mg release
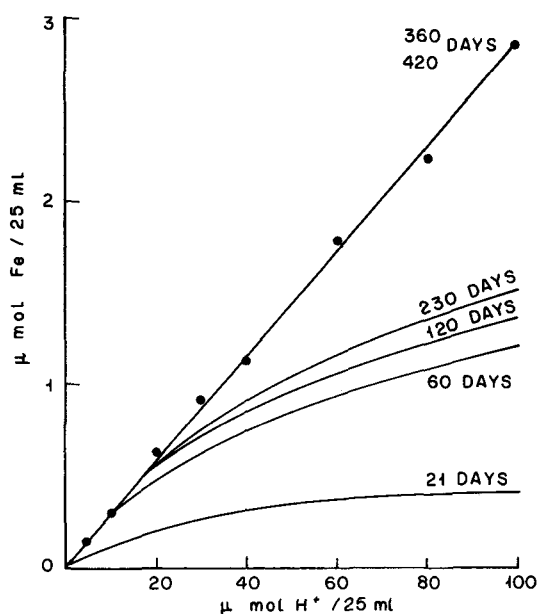

Figure 5. Net dissolution of Al from Mt. Grainger paly-
gorskite after different reaction times with added acid.

is linear with respect to added acid in both palygorskites. The rate of release, however, differs greatly from one mineral to the other. While with the Mt. Flinders palygorskite, 1.2 μmol Mg were released for each μmol of added H^+, the corresponding release of Mg in the Mt. Grainger palygorskite was 0.47 μmol only.

The releases of Al and Fe were shown to be linear with respect to the added acid in the Mt. Grainger palygorskite only. 0.21 μmol Al^{3+} and 0.029 μmol Fe^{3+} were released for each μmol H^+ added (Table 2). The equilibrium pH values in the Mt. Flinders palygorskite suspension were too high for the full equilibrium solubility levels of Al and Fe to be achieved.

The release rates of Mg and Si from the Mt. Flinders palygorskite as a function of added acid were about similar during the initial periods of dissolution (Figures 1 and 3). Between 120 and 230 days the rate of Si release exceeded that of Mg, but while after 270 days equilibrium in Si release was reached, Mg release continued up to 360 days.

The initial Si release from the Mt. Grainger palygorskite lagged somewhat behind that of Mg (Figures 2 and 4). After 120 days, however, the rate of Si release increased to nearly double that of Mg. As with the Mt. Flinders palygorskite, Si release stabilized after 270 days, while Mg release continued for a considerable time afterwards, up to 360 days.

The rates of Al and Mg release from the Mt. Grainger palygorskite were similar during the initial periods of dissolution (Figures 4 and 5). After 60 days the rate of Al dissolution decreased considerably relative to that of Mg and, at equilibrium, was less than half that of the latter.

At equilibrium with the highest concentrations of added acid, 11.2% (molar composition) of Si (as extra-

Table 2. Molar chemical composition of the solid phase palygorskites and their equilibrium solutions

| | μmol in 50 mg solid | | Dissolved by 100 μmol H$^+$ | | | |
| | | | Mt. Flinders | | Mt. Grainger | |
	Mt. Flinders	Mt. Grainger	(μmol)	(%)	(μmol)	(%)
SiO_2	587.	610.0	66	11.2	66	10.8
Al_2O_3	33.5	69.0			20.8	30.1
MgO	200.0	125.0	120	60.0	47.5	38.0
Fe_2O_3	17.5	5.8			2.9	49.3

| | Molar ratio in solid | | Molar ratio in equilibrium solution | |
	Mt. Flinders	Mt. Grainger	Mt. Flinders	Mt. Grainger
Si/Al	8.7	4.4	14.3	3.8
Si/Mg	2.9	4.9	0.67	1.7
Mg/Al	3.0	0.9		2.3
Al/Fe	1.9	11.9		7.3
Mg/Fe	5.7	10.8		16.6

polated from Figure 1), and 60% of Mg present in the undecomposed Mt. Flinders palygorskite, were dissolved (Table 2). From the Mt. Grainger palygorskite 10.8% Si, 14.5% Al, 38% Mg and 24.6% of Fe were dissolved.

The Si/Mg molar ratio in the equilibrium solution of the Mt. Flinders palygorskite was only one-fourth of that in the solid phase (Table 2). The Si/Mg molar ratio in the equilibrium solution of the Mt. Grainger palygorskite was nearly one-third that of the solid phase. This shows that with both palygorskites the dissolution of Mg was strongly favoured over that of Si.

While the rate of Si dissolution is equal in both palygorskites, the rate of Mg dissolution is larger in the Mg-rich mineral, nearly in the proportion of their respective Mg content. It therefore appears that the octahedral Mg is preferentially released into solution over the tetrahedral Si, implying that with progressive dissolution an undissolved Si residue would accumulate, similar to the siliceous "fringes" suggested by Tiller (1968) for the dissolution of hectorite by dilute acid. The development of these fringes might be expected to have an effect on the diffusion of the octahedral Mg through the crystal lattice. Figures 1–4 show that in both palygorskites the Mg dissolution rate decreases relative to that of Si with progressive dissolution time. In an i.r. study, Mendelovici (1973) showed the disappearance of the Si–O–Si absorption band and its replacement by a band characteristic for Silanol groups in HCl treated attapulgite. Whether the "fringe" siliceous residue is actually decomposed into Silanol groups or it preserves the tetrahedral configuration, it seems that it reduces the release rate of Mg from the palygorskite lattice. In this context it is interesting to note that no such reduction was observed for acid-treated hectorite (Tiller, 1968).

As seen in Table 2, the Mg/Al molar ratio in the equilibrium solution is considerably higher than in the solid phase, and less Al than Mg was dissolved
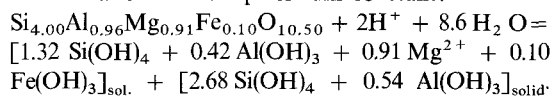
by the highest acid concentration. The difference in the release rate is smaller in the initial dissolution periods, and grows larger during the subsequent ones. Both Mg and Al have octahedral occupancy in palygorskite. Al in tetrahedral positions is unlikely, as shown by strong acid digestion of attapulgite (Abdul-Latif and Weaver, 1969).

Nathan (1968) observed that the process of attapulgite dissolution in dilute acid is selective and much more Mg is removed than Al. The reaction rate constants of Mg and Fe in the dissolution of palygorskite by strong acid were found by Abdul-Latif and Weaver (1968) to be higher than those of Al. Their data corroborate the results of the present study, suggesting that the distribution of Al and Mg in the octahedral sites is not random. The Al/Fe molar ratio in the equilibrium solution of the Mt. Grainger palygorskite is lower than in the solid phase, and relatively more Fe than Al was dissolved by the highest acid concentration. This indicates that both Fe and Mg are preferentially dissolved over Al. Possibly, as Abdul-Latif and Weaver (1968) suggest, the small Al ion is concentrated in more interior positions, while the larger Mg and Fe ions are situated in edge positions. This uneven distribution determines the reaction rates of the different octahedral ions with the acid. As a result, Mg- and Fe- rich palygorskites can be assumed to be far less stable towards weathering and to decompose quicker than the Al-rich varieties.

The evaluation of the stoichiometry of the Mt. Grainger palygorskite dissolution in mild acid and the calculation of the equilibrium constant allow an estimation of the free energy of formation of that palygorskite. It is evident that the free energy of formation value computed in this way primarily reflects the chemical composition of the mineral. Inaccuracies in the determination of that composition will therefore be more critical than errors in the measurement of equilibrium conditions. The structure formula obtained from the chemical composition of the Mt. Grainger palygorskite (Table 1) shows a 0.65 charge

deficiency. In order to obtain an electrically balanced formula, Ca was counted as Mg and some 0.35 charges were distributed among the octahedral cations.

Calculation of the equilibrium constant:

$Si_{4.00}Al_{0.96}Mg_{0.91}Fe_{0.10}O_{10.50} + 2H^+ + 8.6 H_2 O =$
$[1.32 Si(OH)_4 + 0.42 Al(OH)_3 + 0.91 Mg^{2+} + 0.10$
$Fe(OH)_3]_{sol.} + [2.68 Si(OH)_4 + 0.54 Al(OH)_3]_{solid.}$

The solid forms of Si and Al, shown in the acid dissolution equation above, correspond to the undissolved residues that would accumulate after the release of all the Mg, as suggested by the reaction:

$$K = \frac{[Si]^{1.32}[Mg^{2+}]^{0.91}[Al^{3+}]^{0.42}[Fe^{3+}]^{0.10}}{(H^+)^2}$$

and

$\Delta G_R^0 = -1.364 \log K = 1.98 \text{ kcal}$

$\Delta G_R^0 = \Sigma\Delta G_f^0(\text{products}) - \Sigma\Delta G_f^0(\text{reactants}).$

The equilibrium dissolution data in 100μmol H^+, expressed in mol/l are: pSi = 2.58, pAl = 3.08, pMg = 2.72, pFe = 3.92, pH = 3.05. If the solid Si phase is calculated as silicic acid with $\Delta G_f^0 = -312.8$ kcal/mole (Reesman and Keller, 1965), and Al as gibbsite (−274.2 kcal/mole), then the following free energy of formation value for the Mt. Grainger palygorskite is obtained:

$\Sigma\Delta G_f^0 (\text{products}) = -1630.3 \text{ kcal}$
$\Sigma\Delta G_f^0 (\text{reactants}) = \Delta G_f^0 (\text{pal.}) + (-487.5)$
$\Delta G_f^0 (\text{pal.}) = -1630.3 - (-487.5) - 1.98 = -1143.7$ kcal/mole.

Somewhat different values would result if the calculation of the solid phase silica in the "residue would be based on the free energy of formation of amorphous silica.

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