Enhanced Cd(II) Uptake by the Bassanite Phase Contained in Waste Calcite Produced via the Carbonation of Flue Gas Desulfurization (FGD) Gypsum

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The uptake of Cd(II) by waste calcite, a by-product of the carbonation of flue gas desulfurization (FGD) gypsum, was investigated in a batch experiment. The uptake of Cd(II) by and the dissolution of Ca(II) from the waste calcite particles were monitored simultaneously as a function of exposure time to 0.89 mM Cd(II) solution. The reagent-grade calcite particles were also examined for a comparative study. The waste calcite contained bassanite, dolomite, and muscovite as the major impurity phases. X-ray diffraction study revealed that the bassanite phase dissolved almost completely during the 1st hour of the exposure to the solution while other phases were intact for two days. The amount of removed Cd(II) was found to be proportionally related to dissolved Ca(II) reflecting the exchange nature of the adsorption. The use of waste calcite instead of reagent-grade calcite enhanced Ca(II) dissolution and thereby Cd(II) uptake significantly. The waste calcite removed about 90% of initial Cd(II) while reagent calcite removed only 6% during the exposure for 2 days to 0.89 mM Cd(II) solution. The enhanced Ca(II) dissolution and Cd(II) uptake by the waste calcite were attributed to the fast-dissolving bassanite phase which provides the substantial quantity of Ca(II) and sulfate ions to the calcite/solution interface. [doi:10.2320/matertrans.M2011031]

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1. Introduction

Calcite is an environmentally ubiquitous adsorbent for divalent metals, and sorption studies have been performed for natural as well as treatment systems.¹⁻⁵⁾ Among the divalent metals, cadmium (Cd) has attracted the most scientific and practical interest because it is known to have a similar ionic radius to that of Ca (about 98% of that of Ca) and a high sorption affinity to calcite.^{4,5)}

Generally accepted mechanisms involved in calcium dissolution and cadmium adsorption on calcite are explained in terms of the following equations.^{1,5,6)} The dissolution of calcium from calcium carbonate with atmospheric CO₂ gas is established as follows:

Meanwhile, cadmium adsorption on calcite is interpreted as an adsorption at the surface via ion exchange of Cd ions in solution with Ca in solid calcite crystal as follows:

Previous studies on the uptake of cadmium by calcite could be largely divided into two categories from its point of view: understanding of Cd(II) chemistry in a geochemical cycle or application of Cd(II) removal to waste water treatment. In the geochemical sector, specifically refined experimental conditions were employed. For example, solutions pre-equilibrated with calcite and of low Cd(II) concentration were used to minimize the calcium dissolution and to prevent the formation of otavite (CdCO₃) during sorption processes.^{1,6)} Calcite single crystal cleavage surface was often utilized in microscopic studies^{5,7)} to better define the surface chemistry and structure of the sorption products. In addition, the effects of reaction parameters (i.e., temperature, ionic strength, pH, particle size, dissolved species, etc.) on Cd(II) uptake by calcite have extensively studied.^{4,8-11)} On the other hand, at

conditions of conventional water treatment, the uptake of Cd(II) always occurs with the concurrent dissolution of calcite. However, in this case, an emphasis was usually put on the extent of Cd(II) removed.^{2,3,8)}

Gypsum has been produced as a byproduct in flue gas desulfurization (FGD) systems which are applied to control SO_x gas at coal-fired power plants. It is known as FGD gypsum and landfilled as waste though its potential use for the synthesis of ammonium sulfate (a fertilizer) has been documented.^{12,13)}

Calcium carbonate particles can be separated by filtering since the ammonium sulfate exists in dissolved form in aqueous solution as in eq. (1). This waste calcite is known to carry impurities which are retained in FGD gypsum.¹³⁾ It contains impurities as minor carbonate minerals or trace metals which may affect the uptake of Cd(II) to a certain degree. We previously reported the uptake of Cd(II) on the waste calcite giving an attention to a maximum amount and overall kinetic aspect of the uptake.¹⁴⁾ However, we failed to give a specific attention to the effect of minor impurity phases contained in the waste calcite.

The objective of this study was to evaluate the role of major impurity phases contained in the waste calcite on Cd(II) uptake. The extent of removed Cd(II) from and released Ca(II) to the solution was monitored simultaneously. A reagent grade CaCO₃ was also examined for comparison. A relatively high initial concentration (100 mg/L, 0.89 mM) was selected for Cd(II) solution since it is the common value in engineering sorption studies.^{15,16)}

2. Experimental Procedure

2.1 Materials

Cd(II) stock solution (1,000 mg/L) was prepared by dissolving CdCl₂ (Sigma-Aldrich, ACS grade). Ionic strength

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of all solutions was maintained using NaCl (Sigma-Aldrich, ACS grade) and deionized water purified with a Milli-Q 18 M Ω -cm system was used. The cadmium sorption for comparison was conducted with reagent-grade CaCO₃ (Junsei Co.). The adsorbent was prepared from the reaction of FGD gypsum (Yeongheung Thermal Power Plants, Incheon, Korea) with CO₂ gas. The specific surface areas of adsorbents were determined by the BET method of N₂ gas adsorption (ASAP 2010, Micromeritics). The polymorph of the obtained adsorbent and impurity phases were determined using X-ray diffraction (XRD; X'pert MPD, Philips). Scanning electron images of adsorbents were obtained using a field emission scanning electron microscope (FE-SEM; S4700, HITACHI).

2.2 Macroscopic experiments

Batch experiments were performed in duplicate using 100 mg/L of Cd(II) (500 mL) solution and 10 g/L of the adsorbent for 48 h at a temperature of 25 $\pm$ 1°C. Constant ionic strength was maintained using 10 mM NaCl. pH was not controlled but the pH variation during the experiment was insignificant. It was maintained at 7.2 $\pm$ 0.3 between initial and equilibrium time for waste calcite. Especially, for a reagent calcite, pH was rarely varied and stayed at 7.0 $\pm$ 0.1. For the comparison purpose, a reagent-grade CaCO₃ was also tested under identical conditions. The Cd(II) solution was analyzed using ICP-OES (Optima 5300dV, Perkin-Elmer) after filtering through a 0.2 μ m membrane filter (cellulose acetate, Sartorius) and acidifying with instrumental grade HNO₃. Other metal cations except Cd were not detected in a filtrate during sorption reactions. The analytical detection limit for Ca and Cd was 0.02 mg/L and uncertainty was less than 10% with replicates.

3. Results and Discussion

3.1 Characterization of waste calcite

Figure 1 shows the X-ray diffraction patterns of the reagent-grade calcite and waste calcite. The reagent-grade calcite peaks match the standard pattern (JCPDS 47-1743) and do not show any detectable amount of impurity phases. The existence of these minerals could be confirmed by the standard XRD patterns (JCPDS). Since their peaks are very small they should match the largest peak of the standard patterns to be positively identified. The waste calcite consisted of CaCO₃ with second phases as bassanite (JCPDS 45-848), dolomite (JCPDS 36-426), and muscovite (JCPDS 7-25) as marked on the XRD pattern of Fig. 1(b). Here, (a) is the pattern of reagent-grade calcite, (b) is the pattern of waste calcite. On the Fig. 1, B represents bassanite (CaSO₄·0.5H₂O), D represents dolomite (CaMg(CO₃)₂), M represents muscovite (KAl₂Si₃AlO₁₀(OH)₂) and C represents calcite (CaCO₃) phases.

All unmarked peaks represent the calcite phase. The chemical composition of the waste calcite is listed in Table 1. The major impurities determined by XRF were SO₃ (4.63 mass%), SiO₂ (1.91 mass%), and Al₂O₃ (0.85 mass%).

Figure 2 shows the SEM micrographs of the reagent-grade calcite (a) and the waste calcite (b). The reagent-grade calcite had a well-defined rhombohedral crystal morphology with

Fig. 1 X-ray diffraction patterns of reagent-grade calcite (a) and waste calcite (b). Here, B represents bassanite (CaSO₄·0.5H₂O), D represents dolomite (CaMg(CO₃)₂), M represents muscovite (KAl₂Si₃AlO₁₀(OH)₂) and C represents calcite (CaCO₃) phases.

Table 1 XRF analysis of the waste calcite produced by the carbonation of flue gas desulfurization (FGD) gypsum.

Chemical composition	Value (mass%)
CaO	51.64
SO ₃	4.63
SiO ₂	1.91
Al ₂ O ₃	0.85
MgO	0.57
Fe ₂ O ₃	0.41
K ₂ O	0.31
Na ₂ O	0.04
TiO ₂	0.03
P ₂ O ₅	0.02
MnO	<0.01
Ignition loss	39.59

clean surfaces. The waste calcite particles were of irregular shape having a broad size distribution. The difference in particle size was confirmed by BET measurement as well. The specific surface area of the waste-calcite and the reagent-grade calcite were 3.76 m²/g and 0.68 m²/g, respectively.

X-ray diffraction study does not provide enough information on the adsorption product since it is extremely thin. The thickness of the adsorption product is only few tenths of nanometers while X-ray penetrates through tenth of micrometers. Therefore, it is generally not possible to obtain valuable data by conventional X-ray diffraction. The reagent-grade calcite did not reveal any detectable changes before and after exposing them to the solution for 48 h. However, in case of the waste-calcite sample, minor changes in the X-ray diffraction patterns are noticed. Figure 3(a)(b)(c) shows the X-ray diffraction patterns of waste calcite samples after exposing them to the solution for 1 h (b) and 48 h (c) along with the as-prepared condition (a). As previously stated, the waste calcite contained bassanite (CaSO₄·0.5H₂O), dolomite (CaMg(CO₃)₂), and muscovite (KAl₂Si₃AlO₁₀(OH)₂) as its major impurity phases. The dolomite and muscovite peak are seen to remain after the exposure to 0.89 mM CdCl₂ solution for 48 h. On the contrary, the bassanite peaks vanish almost

Fig. 2 FE-SEM images of calcite particles: (a) reagent-grade calcite (b) waste calcite.

Fig. 3 X-ray diffraction patterns of waste calcite: (a) as prepared (b) after the exposure to 0.89 mM CdCl_2 solution for 1 h (c) after the exposure to 0.89 mM CdCl_2 solution for 48 h. Here, B represents bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), D represents dolomite ($\text{CaMg}(\text{CO}_3)_2$), M represents muscovite ($\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$) and C represents calcite (CaCO_3) phases.

completely suggesting that it dissolves rapidly in 1 h. The instant dissolution of bassanite should affect the dissolution of Ca(II) and adsorption of Cd(II) greatly since it provides extra Ca(II) ions to the solution in addition to those from the dissolution of calcite itself. The other two phases are seen to remain intact even after the exposure for 48 h.

3.2 Uptake of Cd(II)

It is important to monitor the extent of not only Cd(II) removed from the solution but also of Ca(II) dissolved into the solution. It was found that the sorption of Cd(II) on calcite crystals was closely related to the dissolution of Ca(II) from the surface. As a matter of fact, this condition was dissimilar to the previous study in that CaCO_3 was stabilized for extended period of time before the addition of Cd(II) ions.⁶⁾ We believe that our experiment represents the conditions more closely the practical wastewater treatment. Their amounts were measured as function of time and presented in Table 2 and Fig. 4. In Table 2, C_0 and C_{48} are the initial

Table 2 Uptake of Cd(II) by the waste calcite and the reagent-grade calcite after the exposure to 0.89 mM CdCl_2 solution for 48 h.

Adsorbent	C_0 (mM)	C_{48} (mM)	$C_0 - C_{48}$ (mM)	U_{Cd} (mmol/g)	U_{Cd}/BET (mmol/m ²)
Waste calcite	0.89	0.0863	0.8037	0.0803	0.0214
Reagent-grade calcite	0.89	0.8362	0.0538	0.0053	0.0078

Fig. 4 Uptake of Cd(II) with time by the waste calcite and the reagent-grade calcite during the exposure to 0.89 mM CdCl_2 solution.

Cd(II) concentration and the concentration after the exposure to the solution for 48 h, respectively. U_{Cd} is the amount of Cd(II) uptake per gram of calcite added and U_{Cd}/BET is the amount of Cd(II) uptake per unit surface area. U_{Cd}/BET was calculated to evaluate the effect of BET surface area on the adsorption and dissolution reactions.

As is obvious in Fig. 4, there was a rapid uptake of Cd(II) during the early hours of adsorption experiment. It then diminishes reaching a limiting value after about 18 h. The fast initial uptake is often observed and interpreted as adsorption while the slow second uptake is explained as precipitation, recrystallization, and/or diffusion into solid for the sorption.^{1,6,17)} After 18 h, further uptake of Cd(II) does not occur at least in a macroscopic scale. This may be due to the unavailability of exchangeable adsorption sites for Cd(II) ions, which prevents further adsorption of Cd(II).

The amount of Cd(II) removed by the waste calcite was significantly higher than that by the reagent-grade calcite. After the exposure for 48 h, about 93% of initial Cd(II) was

Fig. 5 The relationship between dissolved Ca(II) from and removed Cd(II) by the waste calcite in 0.89 mM CdCl₂ solution.

removed by waste calcite (Table 2). On the contrary, the reagent-grade calcite removed only 6% Cd(II). It is possible that the remarkable difference might be originated from the surface area difference. The BET surface area of waste calcite is about 5.5 times larger than that of the reagent-grade calcite. However, the BET surface-area normalized uptake (U_{Cd}/BET) suggests that Cd(II) uptake capacity of waste calcite is still 3 times higher than that of the reagent-grade calcite (Table 2).

3.3 Dissolution of Ca(II)

CaCO₃(s) is thermodynamically stable but it is not a sparingly soluble solid considering the solubility product of calcite ($\log K = -8.4$).⁶⁾ In addition, it reacted in water with atmospheric CO₂ gas ($p_{CO_2} = 10^{-3.5}$) (eq. (1)). It is not clear whether the exchange reaction of Cd²⁺ for Ca²⁺ would proceed simultaneously or subsequently with Ca dissolution.

In view of the generally accepted mechanism that Cd(II) adsorption occurs via the ion exchange reaction of Cd(II) with Ca(II) on the surface of calcite (eq. (2)), it is important to monitor the Ca(II) dissolution with time. At the very beginning of the experiments the aqueous solution is virtually free of calcium, but the concentration increases as the CaCO₃ solids dissolve (eq. (1)).

Figure 5 shows the relationship between dissolved Ca(II) and removed Cd(II) in 0.89 mM CdCl₂ solution for waste calcite. This behavior was similar in the case of reagent-grade calcite but with much less quantity. During the 1st hour of adsorption, Ca(II) dissolved fast to about 3.7 mM removing about 0.3 mM Cd(II). Afterwards, the dissolution of Ca(II) became rather tedious. After about 18 h, both became negligible probably due to the surface coverage of calcite with less-soluble CdCO₃ or (Cd,Ca)CO₃ layer which deters further dissolution of Ca(II).

The dissolution of Ca(II) from the waste calcite was much higher than that from the reagent-grade calcite. Figure 6 shows the dissolution of Ca(II) from the waste calcite and the reagent-grade calcite with time. The initial rapid dissolution of Ca(II) reaches to an equilibrium after 18 h. An easy way to explain the dissolution behavior of two calcite samples would be the surface area difference. Therefore, the effect of the surface area was examined with BET data. Table 3 summa-

Fig. 6 Dissolution of Ca(II) with time from the waste calcite and the reagent-grade calcite during the exposure to 0.89 mM CdCl₂ solution.

Table 3 Dissolution of Ca(II) from the waste calcite and the reagent-grade calcite during the exposure to 0.89 mM CdCl₂ solution for 48 h.

Adsorbent	C ₀ (mM)	C ₄₈ (mM)	C ₄₈ - C ₀ (mM)	D _{Ca} (mmol/g)	D _{Ca} /BET (mmol/m ²)
Waste calcite	0	5.740	5.740	0.5739	0.1526
Reagent-grade calcite	0	0.089	0.089	0.0089	0.0131

rizes Ca(II) dissolution data. Here, C₀ and C₄₈ is the initial Ca(II) concentration and the concentration after 48 h in the solution, respectively. D_{Ca} is the amount of Ca(II) per gram of calcite and D_{Ca}/BET is the amount of dissolved Ca(II) per unit area. D_{Ca}/BET was calculated to normalize the dissolution data with BET surface area. It is seen that the amount of dissolved Ca(II) (D_{Ca}) from the waste calcite is about 64 times higher than that by the reagent calcite. When it is normalized by the BET surface area (D_{Ca}/BET), the dissolved Ca(II) (D_{Ca}) from the waste calcite is still one order higher than that from the reagent-grade calcite. To summarize, the use of waste calcite instead of the reagent-grade calcite increased the Cd(II) uptake and Ca(II) dissolution by 3 fold and 12 fold, respectively. As a matter of fact, in a similar experiment, Prieto *et al.*¹⁸⁾ found that BET surface area was not a good estimate of the reactive surface reaction. Therefore, it is obvious that we should seek an answer other than the high surface area whether BET surface area criteria is appropriate or not in our system.

3.4 Dissolution of bassanite

The waste calcite is known to carry impurities which are retained in FGD gypsum.¹³⁾ The waste calcite used in this study contained major impurities as dolomite (CaMg(CO₃)₂), bassanite (CaSO₄·0.5H₂O) and muscovite (KAl₂Si₃AlO₁₀-(OH)₂). The bassanite phase is likely to be stemmed from a side reaction of the carbonation of gypsum (CaSO₄·2H₂O), and may exist as independent particles.

The bassanite dissolves relatively fast in an aqueous solution. Amathieu and Boistelle¹⁹⁾ investigated the amounts of dissolving bassanite as a function of time. They reported that about 42 g/L of bassanite was immediately dissolved. In our experiment, the amount of bassanite in the waste calcite could be estimated to be 0.463 g/L (5.78×10^{-3} mol/L)

which is far less than a possibly soluble value (3.37×10^{-2} mol/L).¹⁹⁾ The dissolution of the bassanite could proceed according to eq. (4).

The dissolution of the bassanite provides an instant supply of ions (Ca^{2+} , SO_4^{2-}) to calcite/solution interface which can participate in the exchange reaction of Cd(II). The maximum amount of Ca(II) to be dissolved in the waste calcite can be assumed to be 5.78 mM based on the amount of sulfur obtained from XRF analysis. This suggests that 5.78 mM of Ca(II) could be dissolved from bassanite to the solution in addition to Ca(II) from the inherent dissolution of CaCO_3 . The amount is a surprisingly high since it is comparable to the total amount of Ca(II) (5.74 mM) measured after 48 h ($C_{48} - C_0$ in Table 3). If the calculation is correct, then this suggests that most of Ca(II) ions in the solution could be originated from the bassanite. Realizing that significant amount of Ca(II) and sulfate ions are supplied to the solution, the enhancement of Cd(II) uptake should be explained accordingly.

In this respect, the work of Prieto *et al.*¹⁸⁾ is interesting where two aragonite grains and a calcite fragment were used to study the uptake of Cd. There was no second phase dissolution in their system and their aragonite samples contain only 0.5–0.7 mass% impurities other than the calcite. However, they observed that Cd(II) uptake by calcite was lower than that by two aragonites. They attributed the inhibition of Cd(II) sorption on calcite to quicker coverage of the calcite surface by thin epitaxial crystallites which prevent further dissolution of Ca(II) and thus Cd(II) uptake. Even though the same mechanism may work in our system to enhance the uptake of Cd(II), we believe that the fast Ca(II) dissolution from bassanite phase has a more decisive effect.

The effect of sulfate on Cd(II) sorption appears to be inconclusive. Akin and Lagerwerff²⁰⁾ showed that CaCO_3 solubility increased in the presence of sulfate in the solution. Meanwhile, Weijden *et al.*²¹⁾ reported that the sulfate ion suppress the fast initial adsorption of Cd(II) on calcite. We do not have any ground to evaluate the effect of sulfate further since we did not intend and even realize the instant supply of sulfate ion to the solution to begin with.

Obviously, the understanding of the exact mechanism in the enhancement of Cd(II) uptake by waste calcite needs a lot more elaboration and careful study. Nevertheless, it is evident that the enhancement is closely related to the instant dissolution of bassanite which supplies significant amounts of Ca(II) and sulfate ions to the solution changing the chemistry at calcite/solution interface.

4. Conclusions

The uptake of Cd(II) by waste calcite in 0.89 mM Cd(II) solution was investigated in a batch experiment. The waste calcite particles were obtained from the carbonation of FGD gypsum and a reagent grade of calcite was used for a comparative study. The results are as follows:

(1) The waste calcite contained bassanite, dolomite and muscovite as its major impurity phases. The bassanite phase dissolved almost completely during the exposure for 1 h to 0.89 mM Cd(II) solution while dolomite, and muscovite

phases remained intact for 48 h. The instant dissolution of bassanite provided significant amounts of Ca(II) and sulfate ions to the solution resulting in the enhancement of Cd(II) uptake. The maximum amount of Ca(II) to be dissolved from the bassanite phase was assumed to be 5.78 mM based on the amount of sulfur content obtained from XRF analysis.

(2) The Waste calcite removed about 90% of initial Cd(II) while the reagent-grade calcite removed only 6% after the exposure for 2 days to 0.89 mM Cd(II) solution. The uptake of Cd(II) by the waste calcite was significantly higher than that by the reagent-grade calcite even after normalizing the BET surface area.

(3) The uptake of Cd(II) was proportionally related to Ca(II) dissolution. Cadmium was removed fast during the early stage of reaction reaching an equilibrium after about 18 h due probably to the surface coverage by CdCO_3 layer.

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REFERENCES

- 1) J. M. Zachara, C. E. Cowan and C. T. Resch: *Geochim. Cosmochim. Acta* **55** (1991) 1549–1562.
- 2) A. García-Sánchez and E. Álvarez-Ayuso: *Miner. Eng.* **15** (2002) 539–547.
- 3) Ö. Yavuz, R. Guzel, F. Aydin, I. Tegin and R. Ziyadanogullari: *Pol. J. Environ. Stud.* **16** (2007) 467–471.
- 4) M. B. McBride: *Soil Sci. Soc. Am. J.* **44** (1980) 26–28.
- 5) S. L. Stipp, M. F. Hochella Jr, G. A. Parks and J. O. Leckie: *Geochim. Cosmochim. Acta* **56** (1992) 1941–1954.
- 6) J. A. Davis, C. C. Fuller and A. D. Cook: *Geochim. Cosmochim. Acta* **51** (1987) 1477–1490.
- 7) V. G. R. Chada, D. B. Hausner, D. R. Strongin, A. A. Rouff and R. J. Reeder: *J. Colloid Interface Sci.* **288** (2005) 350–360.
- 8) M. Shirvani, H. Shariatmadari, M. Kalbasi, F. Nourbakhsh and B. Najafi: *Colloids Surf. A* **287** (2006) 182–190.
- 9) A. Martin-Garin, P. Van Cappellen and L. Charlet: *Geochim. Cosmochim. Acta* **67** (2003) 2763–2774.
- 10) C. C. Fuller and J. A. Davis: *Geochim. Cosmochim. Acta* **51** (1987) 1491–1502.
- 11) S. K. Thakur, N. K. Tomar and S. B. Pandeya: *Geoderma* **130** (2006) 240–249.
- 12) M.-I. M. Chou, J. A. Bruinius, V. Benig, S.-F. J. Chou and R. H. Carty: *Energy Sources Part A* **27** (2005) 1061–1071.
- 13) W. C. Burnett, M. K. Schultz and C. D. Hull: *J. Environ. Radioact.* **32** (1996) 33–51.
- 14) K. Song, W. Kim, T. Ryu, K.-W. Ryu, J.-H. Bang and J.-N. Jang: *Mater. Trans.* **52** (2011) 224–228.
- 15) Y. Wang, X. Tang, Y. Chen, L. Zhan, Z. Li and Q. Tang: *J. Hazard. Mater.* **172** (2009) 30–37.
- 16) Z. A. Al-Anber and M. A. D. Matouq: *J. Hazard. Mater.* **151** (2008) 194–201.
- 17) C. C. Fuller and J. A. Davis: *Geochim. Cosmochim. Acta* **51** (1987) 1491–1502.
- 18) M. Prieto, P. Cubillas and Á. Fernández-Gonzalez: *Geochim. Cosmochim. Acta* **67** (2003) 3859–3869.
- 19) L. Amathieu and R. Boistelle: *J. Cryst. Growth* **88** (1988) 183–192.
- 20) G. W. Akin and J. V. Lagerwerff: *Geochim. Cosmochim. Acta* **29** (1965) 353–360.
- 21) R. D. van der Weijden, J. Meima and R. N. J. Comans: *Mar. Chem.* **57** (1997) 119–132.