BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2239—2241 (1972)

Fractionation of Oxygen and Carbon Isotopes during Floatation of Calcite

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(Received September 17, 1971)

Fractionation of oxygen and carbon isotopes in systems containing CO_2, HCO_3^-, CO_3^{2-}, and H_2O has been investigated by many workers due to its importance in explaining the isotope variations in natural calcium carbonate deposits.[1–4] In addition to various factors like temperature, source deposition, and equilibrium conditions, the isotopic composition will be affected also by postdepositional exchanges and recrystallisation. If calcium carbonate from a particular site is transported by water to a different location through a process of floatation, the isotopic composition of calcium carbonate at the new site will depend on fractionations involved in the floatation process as well. In the present work oxygen and carbon isotopic compositions of calcium carbonate (calcite) obtained from floatation concentrates and tailings have been determined to see whether any isotopic fractionation occurs during the floatation of calcium carbonate.

Basic principles underlying floatation have been discussed by various authors.[5–7] During floatation, concentration of finely divided material occurs on the variations in their ability to keep themselves on a phase interface. Processess occuring in floatation are based on specific chemical and physical interactions between the various components involved in the system. Froth-floatation has been used to beneficiate the lime content of limestone as well as for removing it out as one of the gangue constituents of other ores. Role of oleic acid as a collector for calcite has been investigated by Lee[8] and Breewood and Miller.[9] Klassen and Kokrousov[6] have given the collecting properties of oleic acid and oleate ions under different conditions. Recently the role of sodium oleate on the floatation of calcite using different collector concentrations and different activators was investigated by Biswas and coworkers.[10,11] They have shown that the recovery of calcite increases with collector concentration, and by using carbon dioxide as the lifting agent instead of air. The nature of acids used to adjust the pH of the pulp before floatation was also found to affect the floatation yield considerably. In the present investigations, calcite from the floatation concentrates and tailings obtained in the presence of hydrochloric, benzoic, citric, and oxalic acids have been used for isotopic studies.

Experimental

Floatation. About 100 g of powdered calcite (−100+200 mesh ASTM) was mixed with about one litre of distilled water. The pH of the solution was adjusted to about 5.7 by the addition of hydrochloric, benzoic, citric, or oxalic acid. Calculated amount of sodium oleate was added so that the concentration was about $2.5—3\times10^{-6}$ mol/*l* in the solution. About 5 m*l* of 5% Dowfroth-250 was added and the pulp was conditioned for about 3 min at an impeller speed of 900 rpm. The pH after conditioning was 6.1 to 6.4. Air was introduced by opening the suction valve and and impeller speed was set to 2100 rpm. Froth was collected and the floatation was over within 3 min. Calcite was collected from the froth (floatation concentrate) and from the solution (tailing), washed, dried, and weighed. Calcite slurry bubbled with carbon dioxide and calcite slurry kept under distilled water also were sampled for isotopic analysis. the experiments were carried out at 27°C. Floatation concentrates and tailings used for isotopic analysis are listed in Table 1.

Isotope Analysis. Samples were decomposed using 100% phosphoric acid according to the procedure of McCrea[1] and the liberated carbon dioxide collected and the yield measured. The isotopic analysis of the carbon dioxide was done on a 6″-60°-RMS-19 double collecting isotope ratio mass spectrometer. The values were corrected as described by Craig.[12] The $^{18}O/^{16}O$ ratio of the carbonate was calculated using the isotope fractionation factor given by Sharma

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Table 1. Description of samples and percentage recovery

Sample No	Description of the sample	% Recovery
R_1	Floatation concentrate, calcite slurry brought to pH 5.7 by the addition of HCl and floated with sodium oleate.	93.5
R_2	Floatation tailings from R_1	
R_3	Floatation concentrate, calcite slurry brought to pH 5.7 by addition of benzoic acid.	95.0
R_4	Floatation tailings of R_3	
R_5	Floatation concentrate, calcite slurry brought to pH 5.7 by the addition of citric acid.	43.4
R_6	Floatation tailings of R_5	
R_7	Floatation concentrate, calcite slurry brought to pH 5.7 by the addition of oxalic acid.	19.0
R_8	Floatation tailings of R_7	
R_9	Calcite slurry kept under distilled water.	—
R_{10}	Calcite slurry bubbled with 3.75 l of CO_2 for 2.5 min.	—

Table 2. Isotopic composition of floatation concentrates and tailings

Sample No	δ ^{18}O (‰) SMOW	δ ^{13}C (‰) PDB	δ ^{18}O[a] (‰) SMOW	δ ^{13}C[a] (‰) PDB
R_1	11.50	−2.83	11.53	−2.81
R_2	12.00	−2.48		
R_3	11.70	−2.57	11.69	−2.55
R_4	11.50	−2.20		
R_5	10.80	−2.65	11.20	−2.52
R_6	11.50	−2.40		
R_7	11.30	−2.80	11.54	−2.95
R_8	11.60	−2.80		
R_9	11.32	−2.70	—	—
R_{10}	11.60	−2.60	—	—

a) Calculated from the following material balance calculation

$$\delta = \frac{\begin{bmatrix}\text{\% yield of}\\ \text{concentrate}\end{bmatrix} \times \delta_{\text{concentrate}} + \begin{bmatrix}\text{\% yield}\\ \text{of tailing}\end{bmatrix} \times \delta_{\text{tailing}}}{100}$$

and Clayton.[13] The isotopic ratios are reported in the delta terminology defined as:

$$\delta = \left[\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1\right] \times 1000 \qquad (1)$$

where $R = {}^{18}O/{}^{16}O$ or $^{13}C/^{12}C$ ratio. The oxygen and carbon isotope values are reported with respect to SMOW (standard mean ocean water) and Chicago PDB carbonate standards respectively. The results of isotopic analyses are presented in Table 2.

Discussion

Factors that can affect the distribution of oxygen and carbon isotopic composition of calcite in the floatation concentrate and tailings are (1) various chemical equilibria involved when calcite dissolves in water, (2) isotope exchange reactions occurring in the solution, (3) solubility of calcium carbonate, (4) relative affinity of various isotopic molecules towards collector anions, (5) pH of the floatation pulp, and (6) temperature. Isotopic fractionation will accompany the several reactions that take place in the system. The various reactions that occur when calcite is placed in water are the following:

$$CO_3^{2-} \text{ (solid)} \rightleftarrows CO_3^{2-} \text{ (aq)} \qquad (2)$$

$$CO_3^{2-} + H_2O \rightleftarrows HCO_3^- + OH^- \qquad (3)$$

$$HCO_3^- + H_2O \rightleftarrows H_2CO_3 + OH^- \qquad (4)$$

$$H_2CO_3 \rightleftarrows H_2O + CO_2 \qquad (5)$$

In a closed system at equilibrium each component will possess characteristic carbon and oxygen isotopic ratios.[3] This is the result of isotopic fractionation occurring between the various components and existence of several exchange reactions of the type:

$$H_2{}^{12}CO_3 + H^{13}CO_3^- \rightleftarrows H_2{}^{13}CO_3 + H^{12}CO^{3-} \qquad (6)$$

$$1/3\, C^{18}O_3^{2-} + H_2{}^{16}O \rightleftarrows 1/3\, C^{16}O_3^{2-} + H_2{}^{18}O \qquad (7)$$

Relative solubility of calcium carbonate in the solution in presence of different ionic species will change the isotopic composition of solid calcite in the floatation pulp and hence will affect the isotopic composition of calcite in the floatation conecntrate and tailing. Experimental investigations of calcium carbonate solubility have shown that solubility varies with temperature, pressure, added salts, pH, and the total amount of CO_2 in the solution.[14] An increased solubility of calcium carbonate will make the remaining calcite isotopically heavier. The affinity of the collector anions towards the various isotopic molecules will also affect the relative isotopic composition in the floatation concentrate and tailing.

The results in Table 2 show that except in the case when benzoic acid was used to adjust the pH, the floatation concentrate is found to be richer in the lighter isotope. This enrichment of lighter isotopes in the floatation concentrate may be due to the greater affinity of the collector anions towards the lighter isotopic molecules and consequent increase in the lighter calcite particles in the froth. Other factors like differences in the solubility of the light and heavy isotopes and partial dissolution of calcite when it is in contact with water will make the tailings enriched in heavy isotopes due to preferential dissolution of lighter isotopic molecules. Oxygen and carbon isotopic fractions between the solid and the dissolved species also might have caused the observed enrichment in the tailings.

Although we do observe differences in the ^{13}C and ^{18}O contents of the floatation concentrates and tailings, the differences are found to be very small, compared to the equilibrium fractionations in other systems. This is owing to nonattainment of isotopic equilibrium conditions due to short period of time. Since all

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the floatation experiments are over within ten minutes much fractionation cannot be expected. Moreover, since the relative amount of bicarbonate and carbonate ion concentration in the solution is much less compared to the total amount of calcite present in the system, change in isotopic composition due to isotopic exchange and solubility differences will be small. The total $\delta^{18}O$ and $\delta^{13}C$ values calculated from material balance of floatation concentrates and tailings are very close to that of calcite kept under distilled water.

Calcite slurry bubbled with CO_2 is found to be heavier than calcite kept under distilled water. When carbon dioxide is bubbled through the slurry, more calcium carbonate will dissolve to form calcium bicarbonate.

$$CaCO_3 + CO_2 + H_2O \rightleftarrows Ca(HCO_3)_2 \qquad (8)$$

As explained earlier, the lighter $CaCO_3$ particles will undergo preferential dissolution making the remining calcite heavier. The observed enrichment in $\delta^{18}O$ and $\delta^{13}C$ are in agreement with this view.

The foregoing results show that there is isotopic fractionation during the floatation of calcium carbonate. The floatation experiments carried out here were in presence of floatation reagents and may be far from conditions under which floatation occurs in nature. Still, it might be one of the factors which determine the distribution of oxygen and carbon isotopes in natural calcium carbonate deposits.