RADIOTRACER MEASUREMENT OF ISOMORPHIC SUBSTITUTION, ACCOMPANIED BY SURFACE ADSORPTION OF A TRACE CATION INTO A CRYSTALLINE HOST MATRIX

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Isomorphic substitution, accompanied by surface adsorption, of a trace cation into a crystalline host matrix from its saturated solution can be studied by a double radiotracer experiment. Recrystallization of the matrix and uptake of the trace cation are thus measured simultaneously. This paper gives the formulation of the radiotracer experiment and the precision with which mole fractions of the trace cation in both phases, may be derived from it. The final result is thus a set of coexisting mole fractions and their uncertainties as a function of time. As an illustration, the case of calcite as the host matrix and Cd$^{11}$ as the trace cation is considered.

Isomorphic substitution of a trace cation into a host matrix from its saturated solution is accompanied by recrystallisation of the solid and surface adsorption. The adsorbed and incorporated amounts of the trace cation and the recrystallized mass of the host matrix are measured as a function of contact time. This yields the ratio of the adsorbed and incorporated amounts of the trace cation and its mole fractions in the two phases as a function of time. The precision of these results can be calculated from those of the radiotracer measurements.

Experimental determination of recrystallisation kinetics with the help of a radiotracer was discussed in a previous communication.\(^1\) It can be supposed that substitution keeps equal pace with recrystallisation. In a previously equilibrated system, the net surface area of the solid does not change with time although it is renewed at a certain rate. Moreover, adsorption will be much faster than substitution. The adsorbed amount of the trace cation will thus be constant over the radiotracer experiment, which focuses on the measurement and its precision of coexisting mole fractions of the trace cation in liquid and solid.

There exists an extensive literature on the application of radiotracers on solid-liquid interactions summarized in (among others) References 2–4. Moreover, the physical chemistry of solid-water interfaces, including recrystallisation and behaviour of traces has been surveyed.\(^5\)\(^6\) The systematics of double radio tracer experiments, as presented here, are not conspicuously available.
Principle

Radiotracer experiments: To a known volume of a saturated solution of the host matrix in a well-defined aqueous medium, in contact with a known amount of the matrix, one adds a known amount of the trace cation and "weightless" spikes of radiotracers of both cations.

The residual fractions of both radiotracers in the liquid are measured as a function of time. For the residual fraction of the matrix radiotracer one has

\[ q_m = \frac{C_m \cdot V}{C_m \cdot V + m_{re}} \]  

or

\[ m_{re} = \left( \frac{1}{q_m} - 1 \right) \cdot C_m \cdot V \]

where \( m_{re} \) is the amount of recrystallized host matrix, \( C_m \) the saturation concentration and \( V \) the volume of the liquid phase (for the symbols their definitions and dimensions see Appendix).

For the residual fraction of the trace cation radiotracer it follows from the mass balance to the trace cation that

\[ q_{tv} = 1 - \frac{(m_a + m_s)}{(C_{tv})_0 \cdot V} \]

with \((C_{tv})_0\) as the original concentration in solution and \(m_a + m_s\) as the sum of the adsorbed and substituted amounts.

Assuming reversible adsorption according to a linear isotherm:\(^2\)

\[ m_a = \alpha \cdot S \cdot (C_{tv}) = \alpha \cdot S \cdot q_{tv} \cdot (C_{tv})_0 \]

it follows that

\[ m_s = (C_{tv})_0 \cdot V \cdot \left[ (1 - q_{tv}) - \alpha \cdot \frac{S}{V} \cdot q_{tv} \right] \]

and thus that

\[ \alpha \cdot \frac{S}{V} = \left( \frac{1 - q_{tv}}{q_{tv}} \right)_{t=0} \]