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Partitioning of Base Metals Between Granitoid Melt and Fluid-Salt and Fluid Phases[1]

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Fluid-magma systems at about 1 kbar fall into a region in which the fluid becomes heterogeneous. Here a concentrated, dense fluid phase, consisting essentially of salt, coexists with a less dense fluid, enriched in water, CO_2 and acid components. Both these phases play a certain role in extracting and transporting ore matter. In this paper, we discuss the results of an experimental study of partitioning of lead and zinc between granite melt and fluid-salt and low-density fluid phases and, from them, consider how ore matter is differentiated in fluid-magma reactions under hypabyssal conditions.

The runs were carried out in a Tuttle-type hydrothermal apparatus at 800° C and 1 kbar for seven to nine days. Ore components were added with the starting solution, as well as with two premelted granite glasses [1] that had the following chemical compositions: a) SiO_2 72.7 percent by weight, TiO_2 0.4, Al_2O_3 13.2, FeO^2 4.2, MgO 0.3, CaO 0.9, Na_2O 2.8 and K_2O 5.9; and SiO_2 75.8 percent by weight, TiO_2 0.2, Al_2O_3 15.3, FeO^2 1, CaO 0.4, Na_2O 3 and K_2O 4.2. Into the capsule were put several pieces of such glass with different concentrations of PbO and ZnO (0.05 to 0.25 percent by weight), wrapped in thin gold foil (d = 0.1 mm). We used starting solutions consisting of H_2O and NaCl and of H_2O, CO_2 and NaCl; CO_2 was added to them as oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) plus hydrogen peroxide, and the metals as $Pb(NO_3)_2$ and $ZnCl_2$. Chlorine was introduced to the starting solutions both as NaCl and as readily soluble $ZnCl_2$, so the total m_{Cl} (in NaCl equivl) was $m_{NaCl} + 2m_{ZnCl2}$. We thereby assumed that adding $ZnCl_2$ in our tests would not substantially change the H_2O-NaCl diagram. The equilibrium of the granite melt with fluid-salt and CO_2-water-fluid phases was studied alternately in different runs; the fluid-phase compositions were close to those coexisting with each other in a heterogeneous fluid. A similar analytical procedure was proposed by other authors [2]. In two runs with the fluid-salt phase, its composition was enriched in MeCl relative to that coexisting with a low-density fluid. Having compared the data of these tests with others on fluids with the sought composition, we do not think that such enrichment substantially affected the results.

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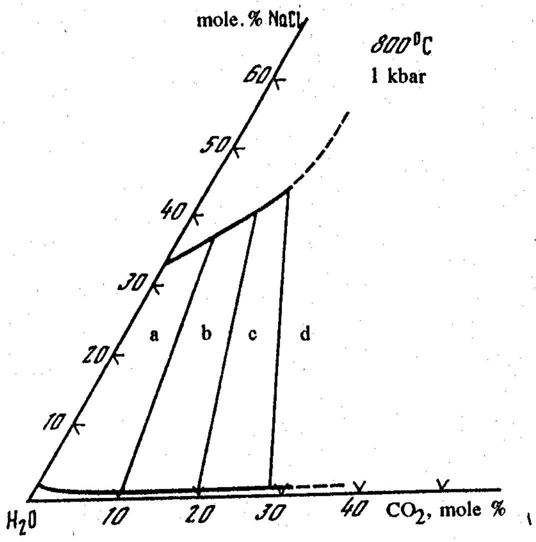

Fig. 1. Schematic phase diagram of part of the H_2O-CO_2-NaCl system. a, b, c and d denote tie lines.

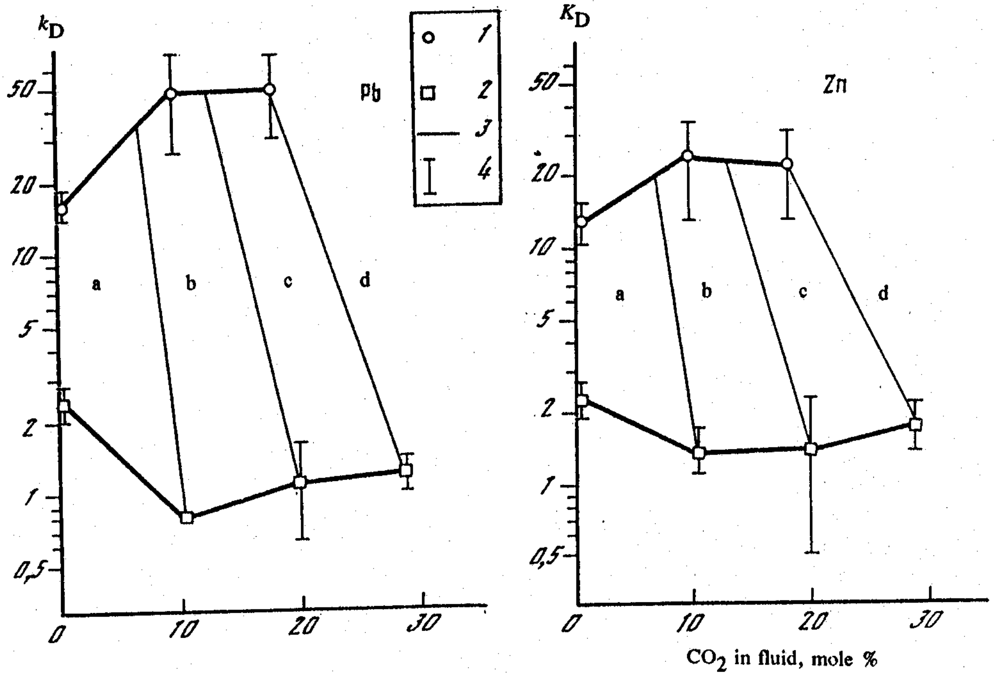

Fig. 2. Partitioning of lead and zinc between fluid phases of different density and granitoid melt: *1*) K_{D1} between fluid-salt phase and melt, 2) K_{D2} between low-density fluid phase and melt, *3*) same tie lines as in Fig. 1, *4*) relative errors of determining K_D.

Table 1

Partitioning of lead between heterogeneous H_2O-NaCl and H_2O-CO_2-NaCl fluid phases and granitoid melt

Starting fluid composition		C_L, % by wt.	C_{fl_1}, % by wt.	C_{fl_2}, % wt. %	K_{D1}	K_{D2}	K_{D3}
mcl(MeCl, mole %)	CO_2, mole, %						
64 (53)	–	0,06–0,08	1,2	–	16 ± 2	–	
0,5 (0,9)	–	0,08–0,11	–	0,23	–	2,4 ± 0,4	6,7
27* (32)	–	0,03**	0,42	–	14	–	
0,4* (0,6)	–	0,03**	–	0,10	–	3	4,7
77 (52)	10	0,02–0,04	1,0	–	48 ± 22	–	
0,5 (0,8)	10	0,28–0,29	–	0,23	–	0,8	41
0,5–0,9 (0,8–1,2)	20	0,23–0,60	–	0,33–0,37	–	1,1 ± 0,5	45
70–79 (46–48)	18	0,02–0,025**	1,0–1,4	–	50 ± 19	–	
0,6 (0,8)	29	0,14–0,18	–	0,19	–	1,2 ± 0,2	42

Note. Here and in Table 2, one asterisk marks runs carried out at 750° C and 1 kb for seven days (fl_1, fl_2 and L were present in one test [8]); two asterisks mark metal concentrations close to the detection limit.

The compositions of starting fluids in the H_2O-NaCl system were taken from the work of Bodnar [3]. At 800° C and 1 kbar, the phases coexisting in equilibrium with each other in a system with C_{NaCl} = 2 to 62 percent by weight contain about 62 percent by weight of NaCl (33 mole percent) and about 2 percent by weight of it (0.6 mole percent), respectively. Little is known about the ternary H_2O-CO_2-NaCl system at high (magmatic) P-T parameters. The phase diagram for part of this system plotted in Fig. 1 is based on data published earlier [3, 4-6]. It shows the broad field in which the fluid-salt and fluid phases separate; the tie lines here (a, b, c, d) join the coexisting phase compositions.

After a run, the metal content near the edge of granite glasses, as well as in the quenching solution, was determined on a Camebax microprobe with a crystal-grating spectrometer. The quenching solution was prepared for analysis by a procedure described earlier [7] and for sizable NaCl concentrations, was modified by adding SiO_2 in the ratio of (3 to 4):12:1 to a mixture of the dry fluid residue and lithium metaborate to guarantee vitrification of the system.

Presented as partition coefficients of the metals studied ($K_D = C_{fl}/C_L$), the results are given in Tables 1 and 2. When a H_2O-NaCl fluid composition is used, a comparison of these data with the results obtained by another method [8], which allowed us to study the partitioning between two fluid phases and a melt in the same test, shows that they are similar, especially for lead. Thus, for a fluid of such composition (without CO_2), the partition coefficient of metals (K_{D1}) between the fluid-salt phase (fl_1) and granite melt (L) proved five to seven times higher than the K_{D2}

Table 2

Partitioning of zinc between heterogeneous H_2O-NaCl and H_2O-CO_2-NaCl fluid phases and granitoid melt

Starting fluid composition		C_L, % by wt.	C_{fl_1}, wt. %	C_{fl_2}, % by wt.	K_{D1}	K_{D2}	K_{D3}
*m*Cl(MeCl, mole %)	CO_2, mole %						
64 (53)	–	0,10–0,14	1,6	–	13 ± 2,5	–	
0,5 (0,9)	–	0,06–0,10	–	0,18	–	2,3 ± 0,4	5,7
27* (32)	–	0,03**	0,25	–	8	–	6,2
0,4* (0,6)	–	0,03	–	0,04	–	1,3	
77 (52)	10	0,02–0,06	0,8	–	24 ± 11	–	
0,5 (0,8)	10	0,18–0,27	–	0,29	–	1,4 ± 0,3	14
0,5–0,9 (0,8–1,2)	20	0,06–0,11	–	0.06–0,14	–	1,4 ± 0.9	16
70–79 (46–48)	18	0,03–0,09	1,3–1,4	–	22 ± 9	–	12
0,6 (0,8)	29	0,08–0,12	–	0,17	–	1,8 ± 0,4	

between the low-density fluid (fl_2) and L. Adding CO_2 to the system increases this difference still more to 45 times for Pb and 15 for Zn. The dependence of K_{D1} and K_{D2} on CO_2 content of the fluid is illustrated in Fig. 2. The tie lines a, b, c and d plotted here are the same as in Fig. 1.

We thought that it would be interesting to express our data as partition coefficients between coexisting fluid phases. Because the partitioning between fl_1 and fl_2 and between fl_2 and L was studied in different runs, the K_{D3} fl_1/fl_2 between the fluid-salt and fluid phases was computed from the formula $K_{D3} = K_{D1}/K_2$. We thereby assumed that over the range studied the K_D fl/L for Pb and Zn is independent of the total content of these metals in the system because their partitioning was different in the runs with fluid-salt and fluid phases. Given this and other assumptions, for example, the arbitrary compositions of coexisting fl_1 and fl_2, the resulting values of K_{D3} between fl_1 and fl_2 must be regarded as approximate.

Note the different behavior of Pb and Zn in the absence of CO_2; the fluid-salt phase is enriched in Pb to a greater extent than in Zn. We may hence assume that in natural fluid-magma systems in the region where a fluid becomes heterogeneous the amounts of Pb and Zn dissolved in the fluid-salt phase are similar, even though the clarke of Pb in granite (20 ppm) is three times lower than the clarke of Zn (60 ppm) [9].

The fact that in the presence of a fluid consisting of H_2O and NaCl for K_{D1} for lead and zinc substantially exceeds their K_{D2} is not surprising and can be explained by the formation of stable chloride complexes in the fluid-salt phase. However, data obtained by adding CO_2 to such fluid are basically new. The supercritical salting out of CO_2 markedly extends the range over which a fluid separates into two components (Fig. 2). In this case, the fluid-salt phase will be substantially enriched, and the CO_2-water-fluid phase depleted in NaCl. But the very substantial increase in K_{D3} when about 10 mole percent CO_2 is added cannot be explained only by such changes in chlorine content of fluid phases. It is interesting here to note the effect of an approximately constant K_{D3} as the CO_2 content of the system further increases (Fig. 2).

Thus, we have experimentally shown that base metals may accumulate in sizable amounts in a fluid phase consisting essentially of salt during liquation of a fluid containing CO_2, chloride and water. This is one of the arguments used to explain the high ore potential of high-temperature fluids. That a high-density fluid-salt phase (≤14 to 40 m Cl) can really coexist with a granitoid melt at magma-type *P-T* parameters has already been demonstrated in various publications [10, 11].

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