Interaction in the systems of fluid–melt–crystal

Salova T.P., Simakin A.G. Transfer platinum dry reduced fluid system $CO\text{-}CO_2$ at p=2 kbar

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Abstract. Transport properties of the reduced carbonic fluid have been studied experimentally at P=2 kbar and T=1000oC. For the studying these properties was used double-capsule technique. In the small capsule was placed carbonates $(Mg,Fe)CO_3$, $FeCO_3$) and sphene, and in a large - albite glass. After the reaction of decarbonization (T>600oC) platinum dissolves, presumably in the form of $Pt(CO)_2$. At the run temperature 1000oC the carbonyl is disintegrate and Pt nuggets are distributed in the albite matrix. In addition to platinum, in the albite matrix were introduced by the Mn, P, REE, and the brought out of the sulfur and strontium. The olivine and aluminous spinel formed in the oxide matrix as a result of the introduction into of SiO_2 and Al_2O_3 fluid CO_2 -CO from the albite melt.

Keywords: reduced carbonic fluid, double-capsule technique, platinum, albite.

Dry fluids with a high content of CO have special properties due to of high ability CO forming π complexes. The transport properties of such fluids are not studied at high PT parameters.

We experimentally study the transport properties of the dry reduced carbonic fluid composition CO_2-CO at P=2 kbar. For the studying these properties was used double-capsule technique.

In a small capsule was placed carbonates: (Mg,Fe) CO_3, $FeCO_3$ and sphene (as the source of impurity elements), and large capsule powder albite glass. Albite glass is used as the fluid trap and the substances dissolved therein.

The decomposition of natural siderite and $FeSO_3$ (Fig.1) formed a mixture of CO and CO_2 with the initial content of 18.8 and 33 mol.%, respectively. The maximum CO content in the mixture was to 21 mol.%. The excess CO was disproportional on CO_2 and carbon.

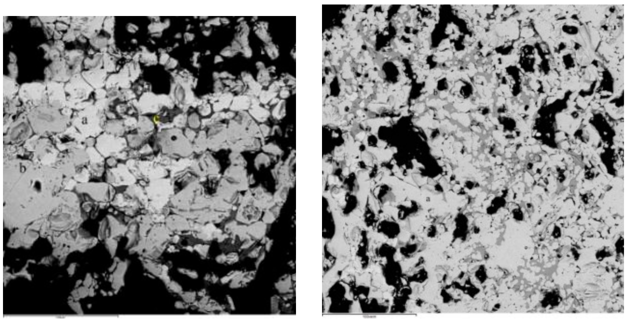

Fig. 1. BSE image of oxide matrix, formed at the decomposition of $FeCO_3$: a) light grey (a) is wustite, grey (b) is magnetite, dark grey (c) is olivine; b) greater inputs of silica from the albite melt has led to an increase in the contents of olivine (gray) and reduction of magnetite (light grey). Wustite is absent.

Platinum (capsule material) is dissolved presumably in the form of $Pt(CO)_2$ after decarbonation reaction and enter albite glass trap placed in the large capsule. As the temperature increases to 1000oC platinum carbonyl decomposed and platinum nuggets (the size of 100-500nm) were distributed in the albite melt. (Fig.2).

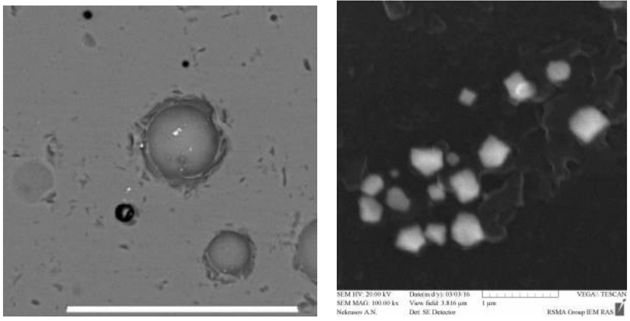

Fig. 2. Platinum in albite glass: a) BSE image of metal particles on the bubbles walls (scale bar 100 mkm); b) the same bubble filmed at high magnification (drawing scale 1 mm).

After isobaric quenching formed glass with bubbles. The fluid composition in the bubbles was studied by the method of Raman spectroscopy (Fig.3). The CO content in the experiments with natural siderite reached 16.5 mol.%. In addition to platinum, in albite glass was introduced by Mn, P, REE, and handed down sulfur and strontium.

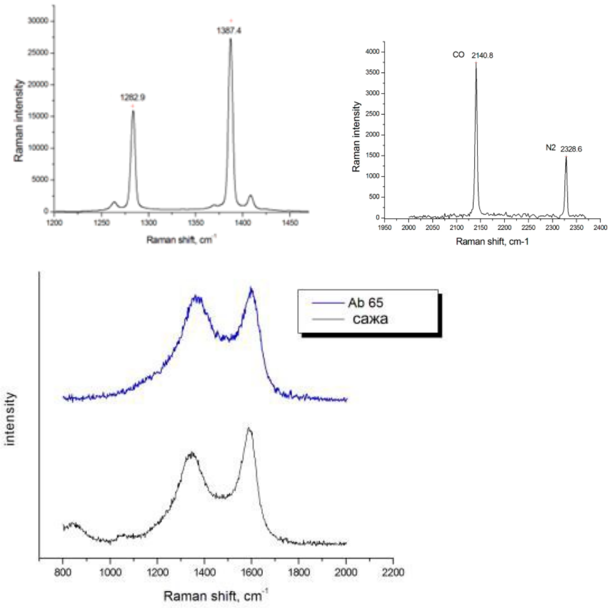

Fig. 3. The Raman spectra of experimental products in the albite glass: a) CO_2; b) CO and N_2; c) spectra of native carbon: upper spectrum is for carbon particle in the albite glass (our data), and lower one is for standard of soot.

Conclusions

1. To study the transport properties of the reduced dry carbon dioxide fluid at P = 2 kbar and T = 700-1000oC used the method of double capsule.
2. After the reaction decarbonization (T>600oC) platinum dissolves, presumably in the form of $Pt(CO)_2$. At T=1000oC the carbonyl is decomposed, and platinum nuggets are distributed in the albite melt. In addition to platinum, in the albite melt were introduced Mn, P, REE, and handed down sulfur and strontium.
3. In oxide matrix formed olivine and aluminous spinel as a result of the introduction into it of SiO_2 and Al_2O_3 of albite melt by fluid CO_2 - CO.

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Partitioning of volatile components (Cl, H_2O, CO_2) between fluids and various magmatic melts at T=1000°C and P=200 MPa

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Keywords: phonolite, dacite, rhyolite, silicate melt, solubility, H_2O, CO_2, Cl, C-O-H-Cl fluids

The dissolution of CO_2-Cl-containing aqueous fluids (0-7 M HCl and from 0 to 20 wt.% ethane diacid) in phonolitic, dacitic and rhyolitic melts was investigated experimentally at T=1000°C, P=200 MPa. After the experiment the composition of the glass and the Cl content in the melt were determined by electron microprobe. The H_2O content in these glasses was analyzed by KFT method. The mole fractions of H_2O and Cl in the fluid were calculated by mass balance method. The results of experiments with CO_2-Cl-containing aqueous fluids were compared with the data of similar experiments in CO_2-free systems.

It is shown that the Cl content in the melt increases significantly from rhyolite (up to 0.25 wt.%) to phonolite (up to 0.85 wt.%), dacite (up to 1.2 wt.%) and andesite (up to 2.8 wt.%) melts. This fact is primarily associated with increased Ca content and possibly Mg and Fe in the melt (Chevychelov, 1999; Chevychelov, Suk, 2003).

For all investigated melts the Cl content in the melt increases with addition of CO_2 in the system. With the rising of the total Cl content in the fluid this increase is amplified. We can assume that the activity of Cl in the fluid increases in the presence of CO_2. As a result of Cl content in the melt increases.

Adding the CO_2 in the system also has a significant influence on H_2O content in the aluminosilicate melts. So the H_2O content in the melt can be reduced on ~0.5-1.0 wt.% at the addition of CO_2. Reducing of the H_2O content in the aluminosilicate melt with the addition of CO_2 is likely explained by the dilution of the fluid by carbon dioxide. As a result of the mole fraction and fugacity of H_2O in the fluid decrease.

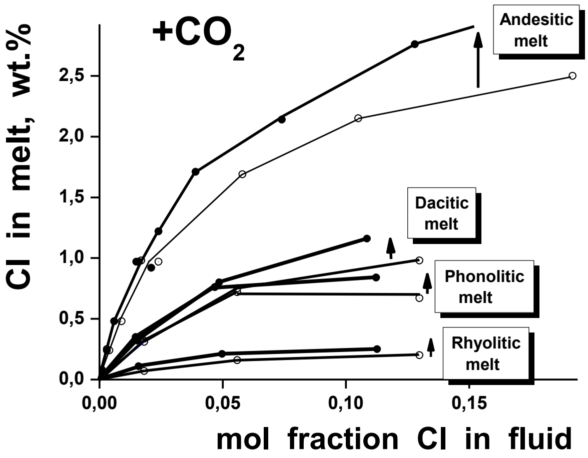

Fig. 1. Melt composition influence on the content of Cl. The effect of adding CO_2. Our data are for dacite, rhyolite and phonolite melts and literature data (Botcharnikov et al, 2007) are for andesitic melt.

The CO_2 contents in the melts in accordance with the data (Behrens et al., 2009) were probably quite low (less than 0.1 wt%).

It should be noted that at lower content of H_2O in the system and the melts undersaturated with aqueous fluid, the solubility of CO_2 in the system phases and possibly the influence of CO_2 on the behavior of other volatile components can grossly change, probably upwards.

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Chevychelov V.Yu. Change of Nb/Ta ratio in granitoid melts depending on the composition of dissolved Ta-Nb mineral and melt composition

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Keywords: columbite, tantalite, silicate melt, granite, solubility, Ta-Nb minerals, Nb/Ta ratio

The dissolution of (Mn,Fe)(Ta,Nb,Ti)$_2$O$_6$ minerals (natural columbite and tantalite-columbite) in three model water-saturated granitoid melts (alkaline, subnormal and alumina-rich) was experimentally investigated at T= 650, 750 и 850°C and P= 100 MPa in the presence of 0.2n HF solution. The starting weight ratio of HF solution / (glass+mineral) was 0.01-0.06.

It is shown that effect of the melt composition (variations of alkaline-alumina ratio) on Ta and Nb contents in the melt is stronger than effect of temperature (Fig. 1). With changing of the melt composition from alkaline to alumina-rich the total Ta and Nb contents in the melt are reduced by 1-2 orders of magnitude and concurrently the Nb/Ta ratio are reduced appreciably. At solubility of columbite in the alkaline melt the Nb content is higher than Ta one. At dissolution of columbite in the alumina-rich melt the Ta predominates already over the Nb. Concurrently the Nb/Ta ratio changes from 2.5-1.8 in the alkaline melt to 0.4 in the alumina-rich melt (Fig. 2b). At dissolution of tantalite the Ta content in all three melts is higher than the Nb content and the Nb/Ta ratio in these melts decreases from 0.7 (in the alkaline) to 0.1-0.5 (in alumina-rich) (Fig. 2a).

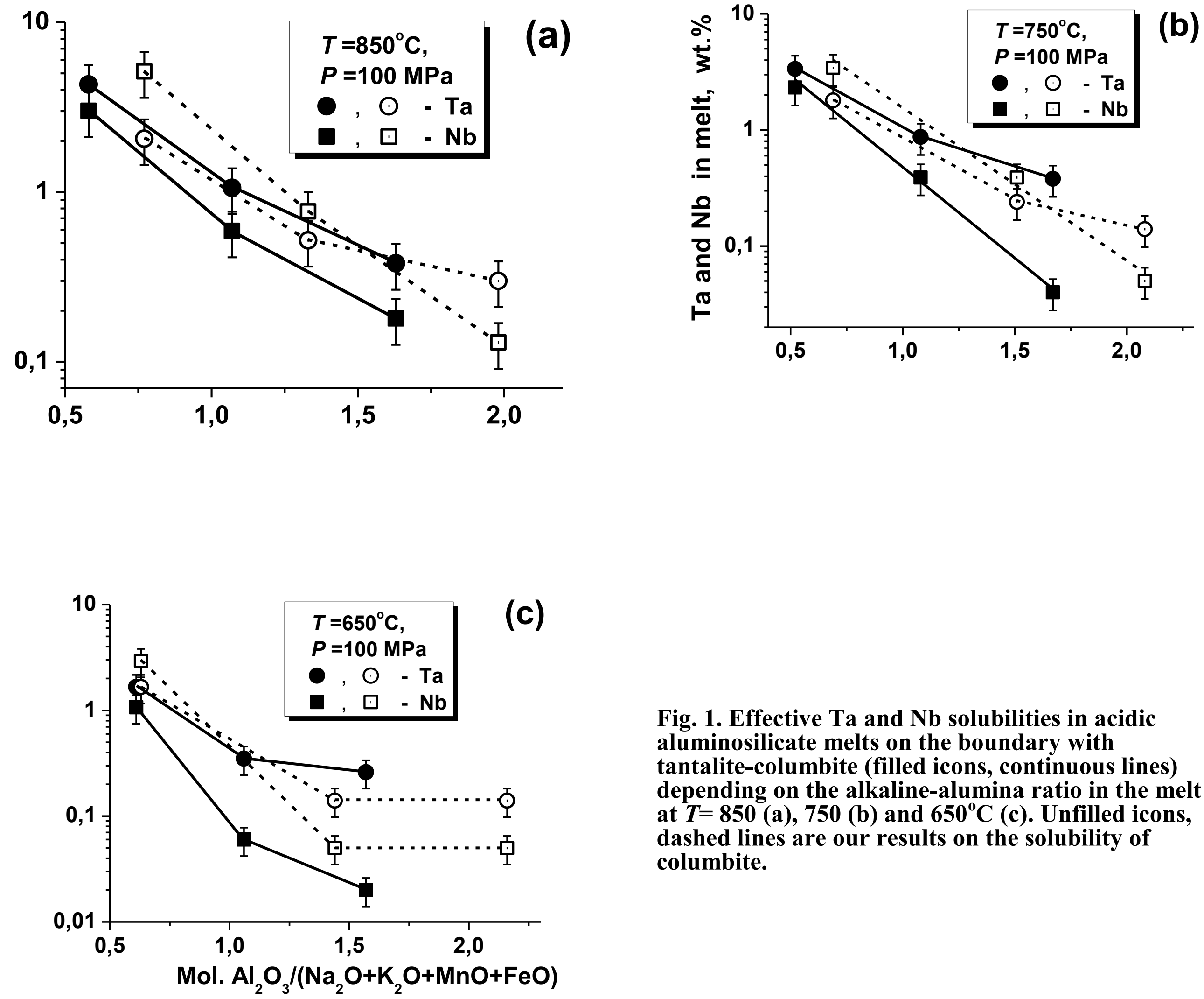

Fig. 1. Effective Ta and Nb solubilities in acidic aluminosilicate melts on the boundary with tantalite-columbite (filled icons, continuous lines) depending on the alkaline-alumina ratio in the melt at T= 850 (a), 750 (b) and 650°C (c). Unfilled icons, dashed lines are our results on the solubility of columbite.

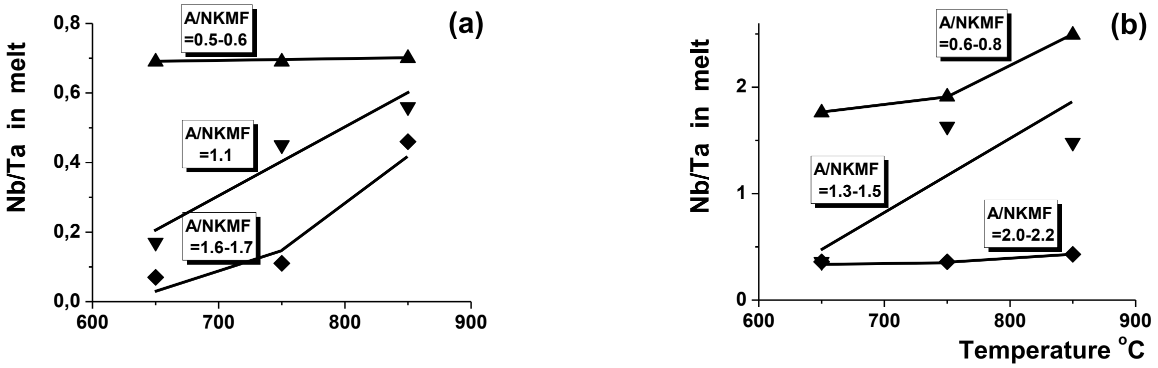

Fig. 2. The weight Nb/Ta ratio in the melt depends on temperature in the experiments on dissolution of tantalite-columbite (a) and columbite (b). Different icons and lines correspond to the three melt compositions: alkaline (A/NKMF=0.5-0.8), subnormal (A/NKMF=1.1-1.5) and alumina-rich (A/NKMF=1.6-2.2).

The reported study was funded by RFBR according to the research project № 15-05-03393-a and DES RAS program "Complex research on topical problems of Earth Sciences."