The role of impurity atoms in forming cation vacancies in the pyrrhotite

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Synthetic pyrrhotites (Fe$_n$S) not containing interstitial atoms in the crystal structure and natural pyrrhotites of the 'Blagodatny' mine containing interstitial point defects have been investigated in the stable phase The phase and chemical composition was monitored by using the methods of X-ray diffraction (XRD) and X-ray spectrum analysis (XRS).

As a result of comparison of the crystal structure and the phase composition of the synthesised samples with natural pyrrhotites the influence of the inclusion atoms on the concentration of cation vacancies has been established.

The influence of impurity atom on the concentration of the cationic vacancies was considered on the basis of calculating the thermodynamic potentials using the Bose-Einstein quantum statistics. The theoretical calculations were compared with X-ray analysis data (Table 1).

The results of the X-ray analysis (XRS and XRD)		The results of the theoretical calculations of the number of defect on point of lattice		
S/Fe ratio	defects mass, %	sum of defects	impurity atom	cationic vacancies
1.130	0.160	0.1038	0.0020	0.1018
1.140	0.168	0.1185	0.0021	0.1164
1.147	0.151	0.1284	0.0021	0.1213
1.154	0.176	0.1234	0.0022	0.1212
1.152	0.143	0.1326	0.0022	0.1304
1.160	0.166	0.1389	0.0023	0.1366
1.158	0.155	0.1366	0.0024	0.1342
1.164	0.177	0.1412	0.0025	0.1387
1.164	0.178	0.1411	0.0026	0.1385
1.157	0.186	0.1363	0.0028	0.1335
1.180	0.415	0.1529	0.0062	0.1467

Table 1. Results of theoretical calculations on the basis of X-ray analysis of samples (XRS and XRD).

As it is shown in the table, tendency to increase of concentration cationic vacancies with increase impurity atom is calculated on the basis of experimental results.

The influence of S on silicate melt structure: An experimental and spectrocospic approach

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Sulfur is one important volatile element after C and H in magmatic systems, however its effects on silicate melt structure and magmatic physical properties are poorly addressed. We present preliminary result of the effect of sulfur on silicate melt structure based on an experimental approach and spectroscopic measurments.

Glasses of HPG8 and An-Di eutectic compositions were synthesised at 300 MPa and 1250°C and under oxidising conditions (ΔFMQ+3.0) using IHPV. Starting compositions were equilibrated with a fluid phase composition: S (0 to 5 wt.%) and H_2O (5 wt.%). Recovered glasses were characterised using EMPA to determine S solubility, FTIR for H_2O solubility, Raman and Solid State NMR for glass structure.

S solubility determined in glasses changes from 0 to 1100 ppm and 0 to 8700 ppm for HPG and An-Di, respectively. The increase in S solubility is accompanied by the decrease in the H_2O content from ~5 to 4 wt.% H_2O. S is directly correlated to the initial S content traducing the change in the fluid phase composition.

Analyses of fluid inclusions suggest S is present as SO_2 and metallic S in HPG and An-Di glasses and additional H_2S has also been identified in some inclusions for An-Di glasses. The S speciation within the glasses is only represented by $M^{n+}SO_4$ groups (M^{n+} is Ca^{2+} in An-Di, Na^+ in HPG) consistent with the oxidising conditions of the experiments.

Raman and NMR analyses of the glass structure show subtle changes upon S dissolution. We observe 1) a slight polymerization with increasing S content, 2) a decrease in ^{VI}Al in An-Di and 3) a change in the H environments with increasing S content. The observed changes may be the result of decreasing H_2O content. However, the subtles changes remain very small suggesting that S will produce only minor changes to the melt strucutre in comparison to H_2O effect. Hence, the change in magmatic viscosity upon S dissolution is likely to be small.