## Experimental investigation of the Fe2O3-As2O5 system in air

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Arsenic is notoriously harmful to the environment. In numerous deposits and mining concentrates, it is usually present in the form of sulfides such as arsenopyrite (FeAsS) and enargite (Cu<sub>3</sub>AsS<sub>4</sub>), arsenides such as loellingite (FeAs<sub>2</sub>) and nickeline (NiAs), arsenates such as scorodite (FeAsO<sub>4</sub>·2H<sub>2</sub>O), annabergite (Ni<sub>3</sub>)  $(AsO_4)_2 \cdot 8H_2O)$  and erythrite  $(Co_3(AsO_4)_2 \cdot 8H_2O)$  and solid solution in ore minerals such as chalcopyrite (CuFeS<sub>2</sub>), pyrite (FeS<sub>2</sub>), and sphalerite (Zn, Fe)S, for example. Currently, scorodite is the mineral of choice to immobilize arsenic from mine wastes because it has a very low solubility in water. Scorodite is also the most common arsenate known in nature where it is found in hydrothermal deposits and as a secondary mineral in gossans. Unfortunately, there is a lack of information in the literature regarding arsenate systems, which hamper the understanding of the complex chemical reactions involved in their genesis. In the last decades, much effort has thus been devoted to determine the thermodynamic properties and phase relations of arsenates in hydrous and anhydrous conditions. In this regard, the Fe<sub>2</sub>O<sub>3</sub>-As<sub>2</sub>O<sub>5</sub> system is of particular interest because it contains the compound FeAsO<sub>4</sub>, the anhydrous analog of scorodite. Surprisingly though, the system Fe<sub>2</sub>O<sub>3</sub>-As<sub>2</sub>O<sub>5</sub> is still poorly known. This is due to the hygroscopic nature, slow kinetics, and high volatility of its phases, and to the presence of iron, which prevent the use of platinum crucibles at high temperature. The first (and only) experimental investigation of the whole phase diagram was performed by Kasenov and Mustafin [Russ. J. Inorg. Chem. (Engl. Transl.), 1997, 42, 1598-1599] using differential thermal analysis (DTA) and X-ray diffraction (XRD) up to 1100 °C. Unfortunately, experiments were performed in sealed but evacuated (to 10<sup>-6</sup> bar, i.e. 10<sup>-3</sup> mm Hg) silica crucibles and as a result, evaporation probably occurred during the runs. Moreover, the silica crucibles may have reacted with the starting materials, modifying the melting point of the solid phases and the oxidation state of both As and Fe in the system. Consequently, the experimental data collected by Kasenov and Mustafin (1997) may have produced a very different phase diagram than the one expected in air. To determine the correct Fe<sub>2</sub>O<sub>3</sub>-As<sub>2</sub>O<sub>5</sub> phase diagram in air and minimize most of the problems cited above (hygroscopicity, slow kinetics, high volatility, and presence of Fe reacting with crucibles), we prepared dry starting materials, carried out long duration experiments (up to 36 days) with non-evacuated sealed Au<sub>75</sub>Pd<sub>25</sub> crucibles up to 1000 °C using the quenching method and accomplished phase characterization using XRD, backscattered electron (BSE) imaging, and electron probe microanalysis (EPMA). Based on our experiments, new subsolidus phase relations are proposed for the Fe<sub>2</sub>O<sub>3</sub>-As<sub>2</sub>O<sub>5</sub> phase diagram in air, which are significantly different from the ones published earlier by Kasenov and Mustafin (1997). We also report the existence of a new compound, Fe<sub>6</sub>As<sub>4</sub>O<sub>19</sub> (F<sub>3</sub>A<sub>2</sub>), which is a potential candidate for arsenic sequestration.

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