Li-extraction from triphylite

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The phosphate minerals triphylite ($LiFePO_4$) and lithiophilite ($LiMnPO_4$) belong to the sequence of primary phosphates which crystallize during the late stage of pegmatite formation. Triphylite and lithiophilite are isotypic (olivine type) and form a complete solid solution in nature. During cooling of the pegmatitic system triphylite – lithiophilite undergoes a chemical reaction with the fluid resulting in extraction of Li and oxidation of Fe^{2+} and Mn^{2+} according to:
$\frac{1}{4}\,O_2 + LiFePO_4 \Rightarrow FePO_4 + \frac{1}{2}\,(Li_2O)_{aq}$ and
$\frac{1}{4}\,O_2 + LiMnPO_4 \Rightarrow MnPO_4 + \frac{1}{2}\,(Li_2O)_{aq}$
The educts and product of this reaction are the members of the so-called Mason-Quensel-sequence minerals. This includes the fully oxidized heterosite – purpurite $(Fe^{3+},Mn^{3+})PO_4$ solid solution as well as intermediate phase ferrisicklerite - sicklerite $(Li{<}1(Fe^{3+}Mn^{2+})PO_4$ [1]. Our study aimed in determination of temperature conditions and oxygen fugacities under which the oxidation of Fe and the extraction of Li occur under geologically relevant conditions. As starting material $LiFePO_4$ (Triphylite) was used which was synthesized in a silica glass ampoule from Li_3PO_4 and $Fe_2(PO_4)_3$ at 800°C. The triphylite was placed in an inner Teflon tube of a sealed hydrothermal autoclave together with diluted HCl plus varying amounts of an oxidizing agent (e.g. $KMnO_4$) and then heated to temperatures between 120 and 170°C. Run durations lasted for one to four weeks. According to XRD under the applied conditions triphylite was completely reacted to the solid phases heterosite ($FePO_4$) + Li_3PO_4. The lattice parameters of the heterosite: a = 0.9812(1), b = 0.5786(1), c = 0.4782(1) nm agreed well with those given by [2] for delithiated $FePO_4$. ^{57}Moessbauer spectroscopy revealed complete oxidation of Fe^{2+} to Fe^{3+}.

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Water solubility in phonolite melts - Influence of melt composition and temperature

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The water solubility in silicate melts is an important parameter for magma evolution and eruption dynamics. Previous studies indicate a great variation in water solubility for phonolite melts [1–3]. It was shown that the water solubility in Na-rich phonolitic melts of Teide and Laacher See volcanoes [1,2] can be 40% higher than in K-rich phonolite melts of Mt Vesuvius [3]. The aim of this study was to elucidate to which extent chemical and physical parameters such as relative amounts of alkali and alkali-earth elements or temperature may be responsible for this variation. To study the effect of chemical composition, a total of 8 different glasses were prepared at 1 atm from mixtures of oxides and carbonates with a base composition of the white pumice of the 79 AD eruption of Mt. Vesuvius. For a series of 4 glasses, the Na/(Na+K) ratio was varied from 0.2 to 0.8. For the other 4 glasses, the (Na+K)/(Ca+Mg) ratio was varied from 2.1 to 10.3, while keeping Na/(Na+K) constant at 0.4. Water solubility experiments were performed at 1200 °C and pressures between 500 and 3000 bars in an internally heated pressure vessel.

First data suggest that both chemical variables have an effect on the water solubility in phonolite melts. However, their influence is not large enough to explain the range of water solubility reported previously. For instance, at 2 kbar, 1200°C an increasing Na/(Na+K) ratio from 0.2 to 0.8 leads to an increase in water solubility of about 0.4 wt% (5.55 to 5.95 wt%). A similar effect is observed by increasing the (Na+K)/(Ca+Mg) ratio from 2.1 to 10.3. The effect of temperature was investigated for a phonolite composition, representative for the Montana Blanca pumice deposit, Tenerife, Canary Islands [1]. Preliminary data for 2 kbar suggest a strong negative temperature dependence with water solubilities of about 6.9 and 5.7 wt% at 850 and 1200 °C, respectively. These data suggest that the previously reported variation in water solubility in phonolitic melts is a result of the variation of both, melt chemistry and more importantly temperature.

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