Minerals Engineering 125 (2018) 42–49

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Separation mechanism of lattice-bound trace elements from quartz by KCl-doping calcination and pressure leaching

Min Lin*, Zhenyu Pei, Yubiao Li, Yuanyuan Liu, Zhenlun Wei, Shaomin Lei

School of Resources and Environmental Engineering, Wuhan University of Technology, 430070 Wuhan, China

ARTICLE INFO

Keywords:
Quartz
Lattice-bound trace element
KCl-doping calcination
Pressure leaching

ABSTRACT

Trace elements bound in quartz lattice are efficiently removed by KCl-doping calcination and pressure leaching. Removal rate of lattice Al reaches 73.5% when 70.4% of lattice-bound trace elements are removed from quartz sand at optimum conditions. The lattice-bound trace elements in quartz are activated by high-temperature calcination, released during phase transformation from α-quartz to cristobalite, diffused to quartz surface by surface enrichment, and removed by oxidation, chlorination and pressure leaching.

1. Introduction

Lattice-bound trace elements in quartz either substitute for Si^{4+} (Al^{3+}, Fe^{3+}, B^{3+}, Ti^{4+}, Ge^{4+}, P^{5+}) or occur at interstitial channel positions (Li^{+}, K^{+}, Na^{+}, H^{+}, Fe^{2+}) where the ions act predominantly as charge compensators for the trivalent and pentavalent substitutional ions Al^{3+}, Fe^{3+} and P^{5+} (Müller et al., 2012). As shown in Fig. 1, theoretical configuration of these trace elements in the quartz lattice mainly includes simple substitution (Ti^{4+}or $Ge^{4+} = Si^{4+}$), coupled substitution ($Al^{3+} + P^{5+} = 2Si^{4+}$), silanol groups ($4H^{+} = Si^{4+}$), and substitution with interstitial charge compensator ($Al^{3+} + Li^{+}(Na^{+}, K^{+}) = Si^{4+}$; $B^{3+} + H^{+} = Si^{4+}$; $Fe^{3+} + K^{+} = Si^{4+}$) (Simpson, 1977; Maschmeyer and Lehmann, 1983; Thomas, 2008; Müller and Kochmüller, 2009; Dennen, 1966) (see Fig. 2.).

Müller and Kochmüller, 2009 suggested a refinement of the hypothetical charge neutrality equation, where the atomic ratio of ($Al^{3+} + Fe^{3+} + B^{3+}$) to ($P^{5+} + H^{+} + Li^{+} + Na^{+} + K^{+}$) should correspond to 1 for natural quartz crystals, although it is possible that electron defects caused by vacancies may also contribute to the charge balance. The electron defects have only little contribution to the charge balance on account of determinations of the $(Al^{3+} + Fe^{3+} + B^{3+})/(P^{5+} + H^{+} + Li^{+} + Na^{+} + K^{+})$ ratio in natural quartz (Müller and Kochmüller, 2009).

The most common trace-element related defect center in quartz is the $[AlO_4]^0$ center which is caused by substitution of Si^{4+} by Al^{3+} with an electron hole at one of the four nearest O^{2-} ions (Griffiths et al., 1954). The precursor state for this paramagnetic center is the diamagnetic $[AlO_4/M^{+}]^0$ center with an adjacent charge compensating cation ($M^{+} = H^{+}$, Li^{+}, Na^{+}) in interstitial position. Other common trace-element centers in quartz are associated with the substitutional incorporation of Ti, Ge and Fe (Mackey, 1963; Wright et al., 1963; Rinneberg and Weil, 1972; Weil, 1984 and 1993; Rakov et al., 1985; Stegger and Lehmann, 1989; Mineeva et al., 1994; Plotze, 1995). Aluminium is the most common trace element in natural quartz, in concentrations of up to several thousand μg/g, and can thus be more easily determined by analytical methods than the other elements. If high Al concentrations are detected, then concentrations of Li, K, Na and H will be high as well and possibly also the concentrations of B and P. So the Al concentration in quartz is thus an important quality indicator.

Lattice impurities in quartz are hard to be removed by conventional processing techniques including magnetic separation and flotation (El-Salmawy et al., 1993; Vieira and Peres, 2007; Xu et al., 2013; Wang et al., 2014) because the trace impurity elements cannot be liberated from the host quartz by crushing and grinding. Although chemical leaching using HF is supported to be an effective method to purify quartz, the leaching process only can remove lattice impurities occurred in outer and inner surfaces of quartz. Loritsch and James, 1991 developed a hot chlorination process which is used for removing lattice impurities from quartz, especially for alkali metal impurities. In the hot chlorination process, quartz is heated to temperatures of 1000–1200 °C in a chlorine or hydrogen chloride gas atmosphere. This refining process is suitable to specifically reduce the level of alkali metal impurities which are highly restricted in lamp tubing and semiconductor applications (Haus et al., 2012). Wu (2016) suggested an NH_4Cl-doping calcination process to purify quartz sand at 600 °C. Total content of main impurity elements in quartz concentrate is reduced to 31.07 μg/g. And the process is thought to have great effects on removing Al, Fe, K and Ti from quartz. Removal of the lattice impurities was divided into

---

* Corresponding author.
E-mail address: 13297013624@163.com (M. Lin).

https://doi.org/10.1016/j.mineng.2018.05.029
Received 8 January 2018; Received in revised form 22 May 2018; Accepted 24 May 2018

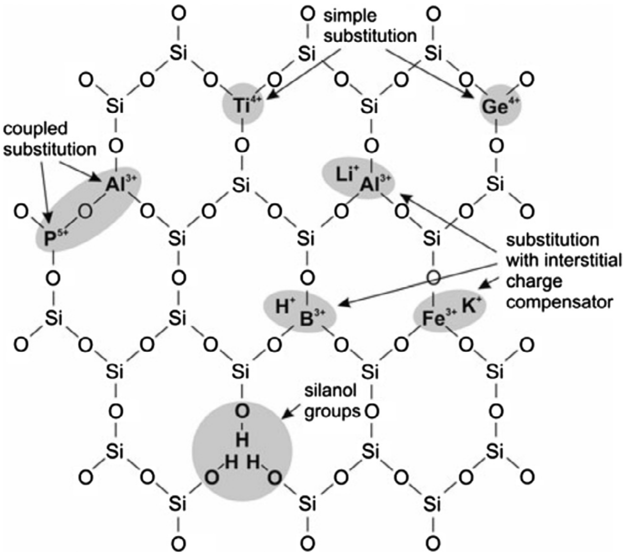

Fig. 1. Schematic quartz structure showing the configuration of trace elements in the quartz lattice (Müller et al., 2012). Because of the two-dimensional illustration the fourth H^+ is not shown on the figure.

three periods including melting of quartz, reacting and escaping of metal chlorides (Wu, 2016). The lattice impurities within semi-vitreous quartz migrate from interior to surface with the constant chlorination of metal ions on quartz surface.

Although acid chlorinating agents such as Cl_2, HCl and NH_4Cl are used for removing lattice impurities during high-temperature calcination of quartz, they would lead to a serious equipment corrosion. Meanwhile, the hot chlorination process extremely demands equipment tightness because of volatility and toxicity of the acid chlorinating agents. Neutral chlorinating agents including NaCl, $CaCl_2$ and KCl perfectly avoid these weaknesses. Yan et al., 2009 presented a NaCl-doping chlorinating calcination process to remove Fe and Ti in quartz. Quartz sand mixed with 2 wt% of NaCl was calcined at 820 °C for 2 h, and the calcined quartz sand was leached by HCl-HF solution at 50 °C. Contents of Fe and Ti were respectively reduced from 66.4 μg/g and 29.3 μg/g to 0.8 μg/g and 5.5 μg/g by the process. Cationic pollution from chlorinating agents should be avoided as much as possible during doping-chlorinating calcination process. Compared with Na^+ (102 pm) and Ca^{2+} (99 pm), ionic radius of K^+ (138 pm) is larger. At high temperature, the K^+ from KCl is more difficult to enter in quartz crystal. Furthermore, Al and K remained in surface and fracture of calcined quartz can be efficiently removed by later pressure leaching process.

This study provides a novel combination process of KCl-doping calcination and pressure acid leaching for effectively removing lattice-bound trace elements from quartz and preparing ultrapure quartz sand. The research is focused on analyzing effects of KCl-doping calcination on removal of trace element Al and lattice structure of quartz, and elaborating separation mechanism of lattice-bound trace elements from quartz.

2. Materials and methods

Quartz ore samples are from a hydrothermal vein deposit in Hengche Town in Qichun County of Hubei Province (China). The bulk quartz was crushed by jaw crusher (PE-Φ100 × 125), and ground by Raymond mill (3R2115). Produced quartz sand ranging from 106 μm (140 mesh) to 212 μm (70 mesh) was selected by standard sieve, and used for purification experiments. The quartz sand (106–212 μm) was calcined at 900 °C for 5 h, and then leached by H_2SO_4-NH_4Cl solution at 250 °C for 6 h (Lin et al., 2017). The processed quartz sand mainly contains SiO_2 and lattice-bound trace elements because mineral impurities included in the quartz have been removed by the process of Lin et al., 2017. The processed quartz sand is experimental material of this study.

Dried quartz materials (100 g per sample) are respectively calcined at 600 °C, 800 °C, 900 °C, 1000 °C and 1200 °C at air atmosphere for 5 h and 45 h, and leached by H_2SO_4-HF solution (0.3 mol/L H_2SO_4, 0.5 mol/L HF, 200 °C, 4 h, 5 cm^3/g of L/S ratio) in pressure-tight reaction kettle. Meanwhile, the quartz materials (100 g per sample) are mixed with KCl (AR, 0.2 g) and ultrapure water (18.2 MΩ·CM, 20 cm^3) in polytetrafluoroethylene crucible, and then dried at 90 °C for 5 h. The dried quartz sands are transferred into transparent silica crucible (200 cm^3, W(SiO_2) > 99.995%), and respectively calcined at 800 °C, 900 °C and 1000 °C for some time in a muffle furnace (KSY-12-16A). The calcined quartz sands are respectively leached by H_2SO_4-NH_4Cl

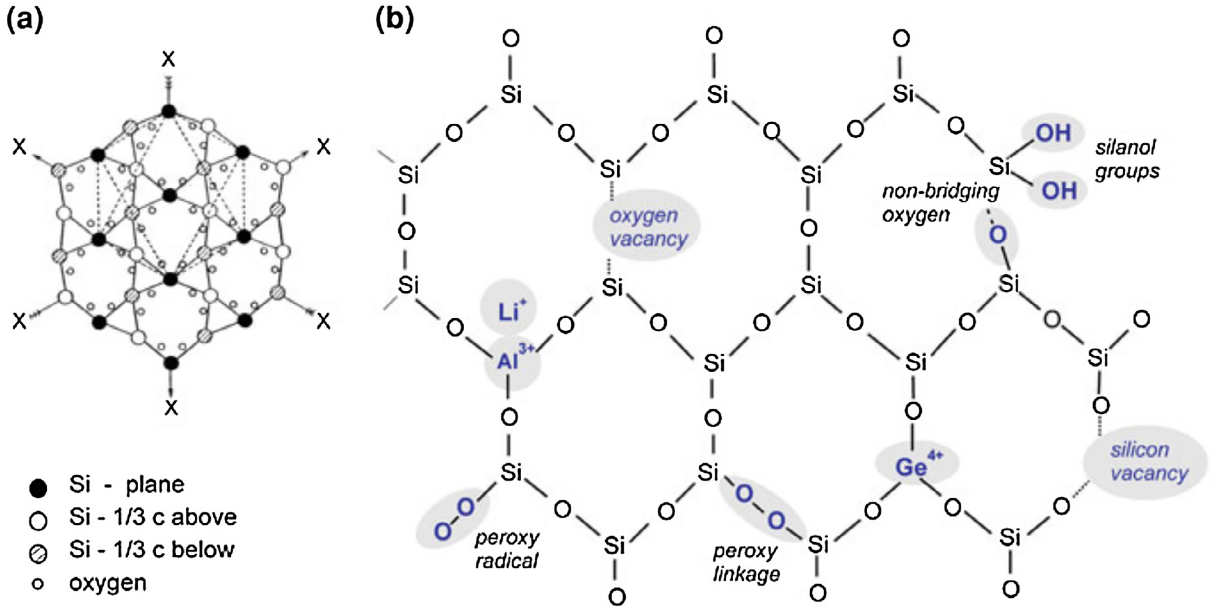

Fig. 2. Schematic structure of a-quartz projected along [0 0 1] showing piezoelectric axes XX (Gotze, 2012).