Morphology, Physicochemistry and Phase Analysis of Neuburg Siliceous Earth

Jürgen Göske and Werner Kachler
Zentrum für Werkstoffanalytik Lauf GmbH, Lauf a. d. Pegnitz, Germany

INTRODUCTION
Polymorphism of Silicon Dioxide
At different conditions of temperature and pressure, silicon dioxide (SiO₂) forms a series of polymorphic modifications of which the most important are with respect to the mineralogical, crystallographic denomination:
- low (alpha) quartz
- high (beta) quartz, tridymite, cristobalite, coesite and stishovite.

Furthermore there still exists a series of rare (lechatelierite, melanophlogite, keatite, etc.) and synthetically produced SiO₂ modifications. The illustration in Figure 1 schematically shows the currently accepted pressure/temperature relationship of stable SiO₂ modifications [1].

At ambient pressure the following modifications exist according to Heaney et al. [2]:
- low quartz up to 573°C
- high quartz from 573°C up to ~870°C
- tridymite from 573°C up to ~1470°C
- cristobalite

The transformation of low to high quartz is called enantiotropy (meaning transferable into each other) and is easily reversible, proceeds very rapidly in a narrow range of temperatures and shows only 1% change of volume. This transformation does not need any de-bonding or the new formation of Si-O bindings. With the exception of high quartz, all crystalline SiO₂ phases and the melt (the so-called undercooled melt) can be generated and maintained in a metastable state at ambient conditions.

At a temperature higher than 573°C originally separated high quartz always exists as low quartz, whereas the morphology of the primary high quartz may be conserved after the spontaneous transformation into low quartz.

As native low quartz appears as well formed crystallites in different shapes, the crystallites of naturally formed high quartz mostly develop hexagonal di-pyramids. The faces of the hexagonal di-pyramids may be shortened significantly or are left totally unchanged (Figure 2) [2].

A Note on Terminology of Quartz
As the use of the labelling alpha and beta quartz or low and high quartz is not standardized within international publications, discrepancies may occur. In former German-language publications the low quartz was called beta quartz, and high quartz was alpha quartz. By contrast, in English-language publications the reverse was the case: the low quartz was called alpha quartz and the high quartz was called beta quartz. In the following article the more logical denominations using Greek figures as alpha (α) for low temperature followed by beta (β) (and so on) for higher temperatures will be used as they have now become more widely accepted [2].

Neuburg Siliceous Earth
The classical Neuburg siliceous earth is a native mixture of corpuscular silica (silica acid) and lamellar kaolinite [4-6]. Both mineral phases become more widely accepted [2].

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MATERIALS AND METHODS
Specimens
The following mineral phases were investigated: 68-79% silica, 15-25% kaolinite, 6-7% accessory minerals (numbers are weight %).

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Neuburg Siliceous Earth
The classical Neuburg siliceous earth is a native mixture of corpuscular silica (silica acid) and lamellar kaolinite [4-6]. Both mineral phases build up a distinctive conglomerate. On the basis of the silica’s fine grain size, its round shaped grain and its naturally aged surface a unique structure of particles is generated.

Figure 1: A pressure/temperature diagram showing the relative stability of SiO₂ modifications [1].

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KEYWORDS
field emission scanning electron microscopy, X-ray diffraction, mineralogy, silica
collected from a quarry in the North of Neuburg an der Donau.

Scanning Electron Microscopy, X-ray Microanalysis and X-ray Diffraction

All scanning electron microscopical analyses were done with a Leo (Carl Zeiss SMT) 1525 field-emission gun SEM which enables high resolution imaging. The SEM was equipped with an EDAX energy-dispersive X-ray spectroscopy system and a Gatan MONO CL cathodoluminescence unit. Further investigations for the exact identification of specimens were done using a PANalytical in-situ X-ray diffraction (XRD) system with an X-Pert Pro system and X'Celerator high-speed detector.

RESULTS AND DISCUSSION

Neuburg Siliceous Earth

The thermo-analytically investigated specimens of Neuburg siliceous earth did not show a quartz transformation behaviour at 573°C, compared with other investigated SiO$_2$ specimens [7].

The investigated specimens of Neuburg siliceous earth definitely contain a combination of amorphous and crypto-crystalline SiO$_2$ modifications (Figure 3).

A precipitated $\beta$-SiO$_2$ modification, originally at temperatures of $>573^\circ$C, always exists as an $\alpha$-SiO$_2$ modification at ambient temperatures, whereas the morphology of the primary $\beta$-SiO$_2$ modification may be conserved after the spontaneous transformation into the $\alpha$-SiO$_2$ modification. Hence the $\alpha$-SiO$_2$ modification exists significantly as a pseudomorphosis to the $\beta$-SiO$_2$ modification in the Neuburg Siliceous Earth (Figure 4).

The morphological proof for the existence of the $\beta$-SiO$_2$ modification was successfully obtained. Well formed, hexagonal di-pyramids could be identified by scanning electron microscopy.

The crystallites of the pseudomorphosis of the $\beta$-SiO$_2$ modification were affixed among each other with an amorphous SiO$_2$ matrix, partially coated opal-like or melted into a mineral entity. Their surfaces were aged and showed an amorphous, opal-like structure.

Cathodoluminescence effects of the SiO$_2$ modifications indicated that they were formed above 573°C and rapidly cooled down.

The Neuburg siliceous earth can neither be even approximately produced synthetically nor by the mixture or ad-mixture of native components of a SiO$_2$ modification with kaolinite.

On the basis of the scientific results – and because of the high degree of disordering of the SiO$_2$ modification – the Neuburg siliceous earth can be characterized as a unique SiO$_2$ modification and so we propose that it may now be called Neuburg silica.

REFERENCES