Morphology, Physicochemistry and Phase Analysis of Neuburg Siliceous Earth

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BIOGRAPHY

Jürgen Göske studied mineralogy at the Friedrich Alexander University Erlangen Nürnberg and completed his Dr. rer. nat. at the Martin Luther University Halle-Wittenberg in the field of applied and environmental mineralogy. Since 2003 he has been the managing director of the Zentrum für Werkstoffanalytik Lauf GmbH. He is now working in the fields of technical mineralogy and materials science using FE-SEM, combined with cathodoluminescence and cryotransfer techniques, clinker microscopy, thin-film measurements and high-speed diffraction.

ABSTRACT

We have investigated Neuburg siliceous earth by means of optoelectronic, physicochemical and phase-analytical methods. The classical Neuburg siliceous earth is a native mixture of corpuscular silica (silica acid) and lamellar kaolinite. Thermo-analytically investigated specimens contain a combination of amorphous and crypto-crystalline SiO_2 modifications and do not show a quartz transformation behaviour at 573°C. 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 may be called Neuburg silica. Neuburg silica cannot be produced even approximately by synthesis or by the mixture or ad-mixture of native components of a SiO_2 modification with kaolinite.

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KEYWORDS

field emission scanning electron microscopy, X-ray diffraction, mineralogy, silica

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INTRODUCTION

Polymorphism of Silicon Dioxide

At different conditions of temperature and pressure, silicon dioxide (SiO_2) 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 SiO_2 modifications. The illustration in Figure 1 schematically shows the currently accepted pressure/temperature relationship of stable SiO_2 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 SiO_2 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].

Neuberg 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.

MATERIALS AND METHODS

Specimens

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

The investigated natural specimens were

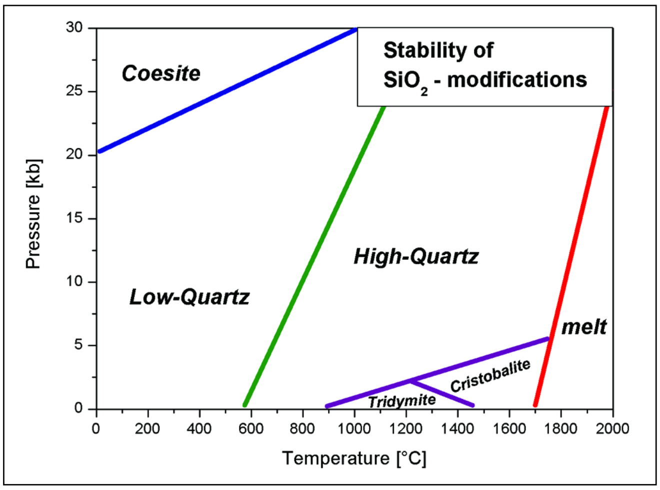

Figure 1: A pressure/temperature diagram showing the relative stability of SiO_2 modifications [1].

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 β-SiO_2 modification, originally at temperatures of >573°C, always exists as an α-SiO_2 modification at ambient temperatures, whereas the morphology of the primary β-SiO_2 modification may be conserved after the spontaneous transformation into the α-SiO_2 modification. Hence the α-SiO_2 modification exists significantly as a pseudomorphosis to the β-SiO_2 modification in the Neuburg Siliceous Earth (Figure 4).

The morphological proof for the existence of the β-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 β-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.

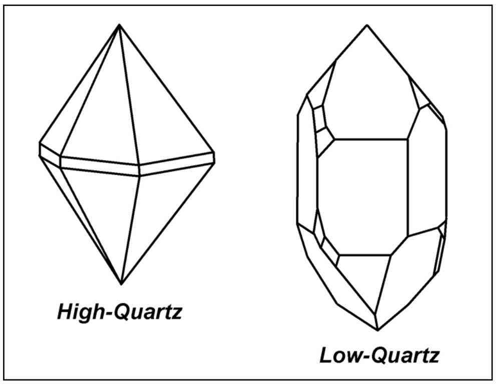

Figure 2:
Typical crystalline morphology of high (beta) quartz (left) and low (alpha) quartz (right) [1].

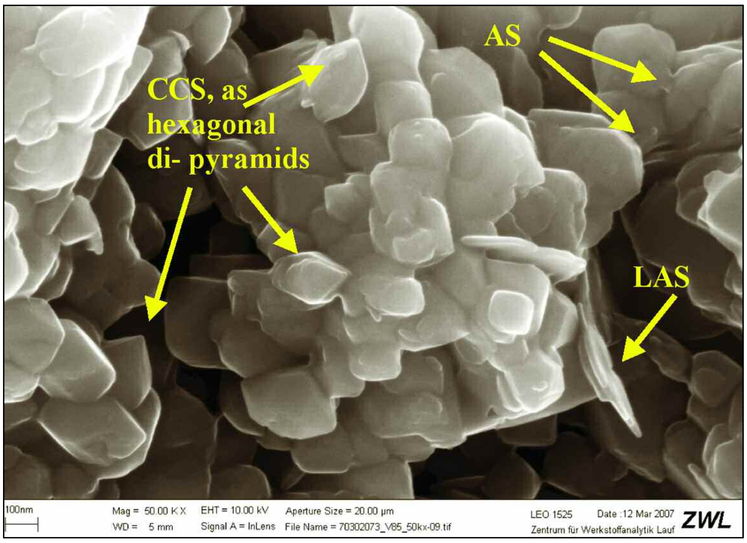

Figure 3:
Scanning electron micrograph of Neuberg siliciceous earth showing that besides crypto-crystalline (CCS) and amorphous (AS) SiO_2 phases there are lamellar alumo-silicates (LAS). No isolated SiO_2 crystallites could be identified; all of them are affixed and stuck together by an amorphous SiO_2 containing matrix, coated opal-like with the amorphous SiO_2 containing matrix.

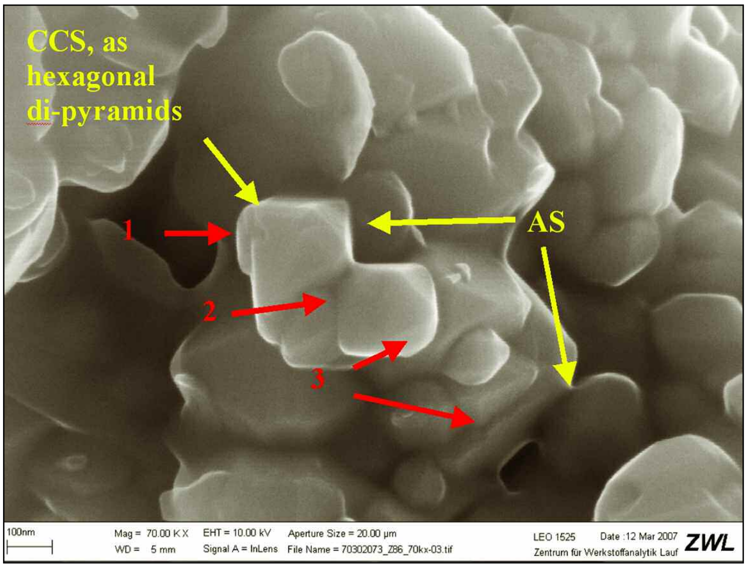

Figure 4:
Single crypto-crystallites (CCS) of the pseudomorphosis of the high (beta) SiO_2 modification stuck together and are affixed by an amorphous SiO_2 containing matrix (AS), partially coated, bonded or molten into a "mineral entity". The faces of the hexagonal di-pyramids may be shortened significantly (1) or are left totally unchanged (2). Single crystallites are aged superficially and show amorphous, opal-like structures (3).

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