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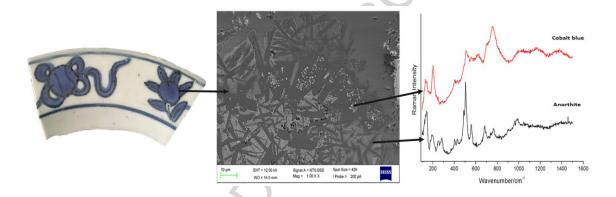


## ACCEPTED MANUSCRIPT

Raman analysis of cobalt blue pigment in blue and white porcelain: a reassessment

Xiaochenyang Jiang  $^{a,b}$ , Yanying Ma  $^c$ , Yue Chen  $^{b,d}$ , Yuanqiu Li  $^{a,b}$ , Qinglin Ma  $^{d,*}$ , Zhaoxia Zhang  $^a$ , Changsui Wang  $^{a,b}$ , YiminYang  $^{a,b,**}$ 

#### **Graphical Abstract**



#### **Abstract**

Cobalt blue is a famous pigment in human history. In the past decade it is widely reported that the cobalt aluminate has been detected in ancient ceramics as blue colorant in glaze, yet the acquired Raman spectra are incredibly different from that of synthesised references, necessitating a reassessment of such contradictory scenario with more accurate analytic strategies. In this study, micro-Raman spectroscopy (MRS) and scanning electron microscopy (SEM) in association with energy dispersive spectrometry (EDS) were performed on under-glaze cobalt pigments from one submerged blue and white porcelain shard dated from Wanli reign (1573-1620 AD) of Ming dynasty (1365-1644 AD) excavated at Nan'ao I shipwreck off the southern coast of China. The micro-structural inspection reveals that the pigment particles have characteristics of small account, tiny size, heterogeneously distribution, and more importantly, been completely enwrapped by well-developed anorthite crystals in the glaze, indicating that the signals recorded in previous publications are probably not from cobalt pigments themselves but from outside thickset anorthite shell. The further spectromicroscopic analyses confirm this presumption when the accurate spectra of cobalt aluminate pigment and surrounding anorthite were obtained separately with precise optical positioning. Accordingly, we reassess and clarify the previous Raman studies dedicated to cobalt blue pigment in ancient ceramics, e.g. cobalt blue in celadon glaze, and in turn

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