

## ARSENIC UPTAKE BY NATURAL CALCITES: PRELIMINARY RESULTS FROM SEQUENTIAL EXTRACTION OF ITALIAN TRAVERTINES

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### Abstract

Natural calcite has received little attention as a mineralogical trap for As, despite the abundance of this mineral on the Earth's surface. Recently, Di Benedetto et al. (2006) demonstrated that the  $\text{CO}_3^{2-} = \text{AsO}_3^{3-}$  substitution is possible in natural calcite hosted by Quaternary travertine deposits in Southern Tuscany, Italy. Two extraction procedures were compared in this study to quantify the arsenic content in the travertine samples studied by Di Benedetto et al. (2006). The two procedures yielded As values ranging from 109 to 270 mg/kg. These results indicate that the  $\text{CO}_3^{2-} = \text{AsO}_3^{3-}$  substitution in natural calcite can be an effective trap for this metalloid.

### Introduction

Arsenic contamination of groundwater and food represents a serious environmental problem in many parts of the world, and has been recognised as one of the major threats to public health (Matschullat, 2000; Smedley and Kinniburgh, 2002). The chemical and physical state of arsenic controls its mobility in the natural environment and, ultimately, its intake in the human food-chain. Much attention has been paid to sorption-desorption and coprecipitation reactions between arsenic and mineral surfaces, especially with Fe- and Mn-oxyhydroxides (Lenoble et al., 2002; Ouvrard et al., 2005; Sherman and Randall, 2003). This is considered the most important and common mechanism controlling arsenic mobility and its potential release into the human food-chain (Nriagu, 1994a, b). The uptake of arsenic in solid phases can remove this metalloid from solution, thus retarding its transport and decreasing its bio-availability (Sposito, 1984; Stumm and Morgan, 1996; Langmuir, 1997). The adsorption of arsenic by Fe- and Mn-oxyhydroxides surfaces, although being highly effective in general, represents only a transient immobilization of this element because, in principle, mineral surfaces could exchange it with other chemical species in solution. Recently, Roman-Ross et al. (2006) have demonstrated that it is possible, under laboratory conditions, to synthesize calcite in presence of high As(III) concentrations. The resulting Ca-carbonate may contain, on average,  $30 \pm 6$  mmol/kg ( $\sim 2200$  mg/kg) of As(III); the metalloid is incorporated in calcite by a solid solution mechanism, with  $\text{CO}_3^{2-}$  ions being replaced by  $\text{HAsO}_3^{2-}$  ions, offering a more stable trap than superficial adsorption.

Natural calcite has received little attention as a mineralogical trap for arsenic, despite its abundance and widespread distribution on the Earth's surface (Cheng et al., 1999; Le Guern, 2003). This is probably due to the fact that natural carbonates do not contain significant amounts of arsenic, and its detection and quantitative determination by conventional analytical methodologies is therefore difficult. However, in a recent EPR-ESE study of an As-rich natural travertine deposit from Southern Tuscany (Italy), Di Benedetto et al. (2006) demonstrated that arsenic may be trapped also by natural calcite. The EPR-ESE spectra suggest that arsenic enters the calcite lattice through the  $\text{CO}_3^{2-} = \text{AsO}_3^{3-}$  substitution, a mechanism that implies a charge imbalance, contrary to what proposed by Roman-Ross et al. (2006). The EPR-ESE spectroscopy does not allow a quantitative determination of arsenic, and therefore the amount of this metalloid that can be trapped by natural calcite is unknown and the actual role that calcite may play in scavenging arsenic from the environment has not been evaluated. To address these questions, we have set up a preliminary experiment aimed at quantifying the amount of arsenic that can be incorporated by natural calcite. The samples were obtained from the travertine sequence studied by Di Benedetto et al. (2006). Two different sequential extraction procedures were tested and compared, because a reliable scheme for arsenic extraction from carbonate rocks is not available in the literature.

### Sampling area and geological outline

Travertines with anomalous arsenic content were sampled in Southern Tuscany in the Pecora River catchment (Fig. 1; Costagliola et al., 2004; Di Benedetto et al., 2006). These travertines are found at the top of a stratigraphic sequence composed mainly of Quaternary clastic sediments filling a basin that formed after the Late Cretaceous-Middle Miocene compressional stages of the Apennine orogeny. They formed in a lacustrine-phytoclastic environment, and are composed by dominant calcite associated with variable amounts of other minerals, including iron oxyhydroxides. Thin centimetric layers of non-carbonate minerals represent cyclic

ingression of siliciclastic materials into the travertine lake. In total we have analysed seven travertine samples belonging to the same stratigraphic column.

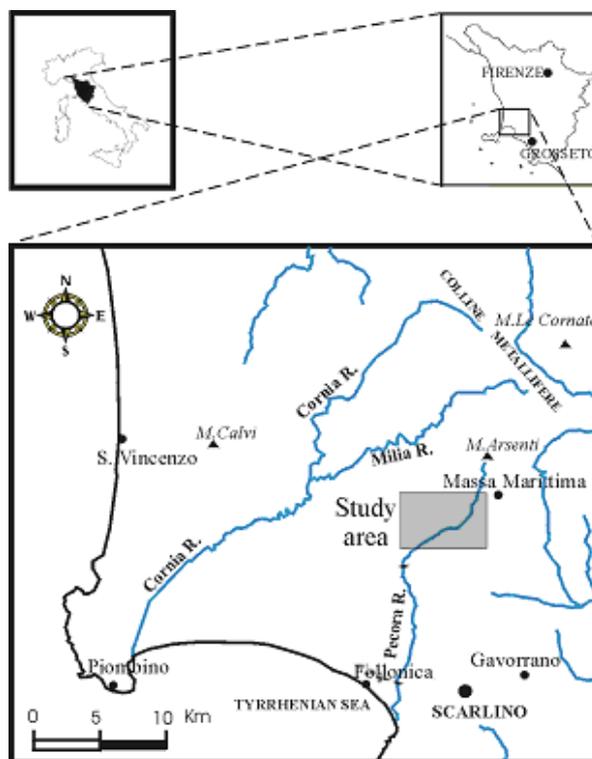


Figure 1. Location of the study area (modified after Costagliola et al., 2004).

### Rationale and Analytical Methods

Many different sequential extraction procedures have been proposed to evaluate the actual amounts of heavy metals (generally cations) bound to specific mineralogical fractions. As far as anions are concerned, as in the case of arsenic, specific procedures are needed which take into account the different geochemical behaviour of anions with respect to cations and to the specific mineralogical matrix of the studied samples (Dold and Fontbotè, 2001; Herreweghe et al., 2003; Matera et al., 2003). Generally, the classical method to recover toxic elements bound to the carbonate fraction includes an acetic acid extraction at a pH of about 5. However, the mineralogy of the travertine samples includes a non negligible fraction of Fe-oxyhydroxydes that could adsorb, at least in part, the arsenic released from calcite during the extraction. At a pH value of 5, arsenic anions are readily adsorbed onto the Fe-oxyhydroxides surface (Drever, 1997). This feature may lead to underestimate arsenic content in the carbonate fraction and to overestimate the metalloid in the Fe-oxyhydroxide fraction.

Recently, Jang et al. (2005) have demonstrated that sodium hydroxide is capable of extracting arsenic from oxide and amorphous aluminosilicates in a very efficient and rapid way. Therefore, to overcome the problems of arsenic extraction from the carbonate fraction using the classical approach, we developed a new method (Procedure A). First, arsenic adsorbed onto Fe-oxyhydroxides was leached using a NaOH solution (pH~12.5) for about 20 hours (Step 1A). Subsequently (Step 2A), the sample was leached using an aqua regia solution to determine the arsenic bound to the carbonate fraction. From the calcimetric analysis of the samples we calculated the amount of calcite, and from this the absolute concentration of arsenic in calcite.

The effectiveness of this procedure was evaluated by comparing the obtained results with the classical procedure (Procedure B), in which the sample was treated with an acetic buffer (Step 1B) to extract the arsenic bound to carbonates, and subsequently leached with aqua regia (Step 2B) to recover the arsenic associated with the Fe-oxyhydroxides.

Arsenic solutions were analyzed by Hydride Generation AAS using a Perkin Elmer AAnalyst100 Spectrophotometer equipped with a Perkin Elmer FIAS 100 Hydride Generator. The analytical quality was

controlled by using international standards. The relative difference between our results and the certified arsenic contents in the standards was <10%.

### Results and Discussion

The arsenic recovered using extraction procedures A and B ranged from 120 to 191 mg/kg, and from 83 to 124 mg/kg, respectively. Based on the calcimetric analyses, the arsenic content in calcite ranges from 137 to 270 mg/kg in procedure A, and from 109 to 156 mg/kg in procedure B. Procedure A yielded As values systematically higher than the "classic" Procedure B, suggesting that the use of the acetic buffer may lead to an underestimation of the arsenic bound to calcite. On average, results of procedure A were 35% higher than those of procedure B.

The reliability of procedure A to estimate the arsenic content of calcite is strongly dependent on the amount of arsenic that calcite may adsorb during step 1A. In principle, if the arsenic released by the Fe-oxyhydroxides after alkaline extraction with NaOH solution is taken up by calcite, this would cause an underestimation of the arsenic bound to Fe-oxyhydroxides (and a corresponding overestimation of the arsenic bound to calcite). The adsorbing behaviour of arsenic onto calcite surface is not well established in the literature. Sadiq (1997) suggested that carbonates may play an important role for arsenic adsorption in soils at pH between 7.5 and 9. At higher pH the adsorbing effect of Ca-carbonates should be minor because the isoelectric point of calcite is at pH ~ 10. More recent studies conducted at pH between 6.0 and 9.5 showed that calcite behaves as a minor adsorbent for arsenates in laboratory simulations of natural water-rock interaction (Le Guern et al. 2003). Goldberg and Glaubig (1988), however, studied the arsenate adsorption on calcite in the pH range between 6 and 12.5, and observed that adsorption increased from pH 6 to 10, peaked between pH 10 and 12, and then decreased for pH > 12. This latter feature may suggest that procedure A (at pH 12.5) may actually overestimate the arsenic content in calcite.

Considering our experimental data and information available from the literature, we estimate that the arsenic content of our calcites is in the range of 150-200 mg/kg. Although this figure is about one order of magnitude less than the amounts incorporated by synthetic calcite (Roman-Ross et al., 2006), it is nonetheless environmentally significant, considering the abundance and diffusion of calcite on the Earth's surface.

### Conclusion

The arsenic content of natural calcites of Quaternary travertines from the Pecora Valley in Italy was measured following extraction with two different procedures. The two procedures gave systematically different (about 35%) arsenic contents, but we were able to establish that the As content of these natural calcites ranges from 150 to 200 mg/kg. Although synthetic calcite can contain much larger amounts of arsenic than our natural samples, our study indicates that calcite may play an important role in arsenic immobilization in natural systems.

### Acknowledgements

This work was supported by Università di Firenze through research funds (ex-60%) to P. Costagliola and M. Benvenuti.

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