A statistical reassessment of the evidence for the racemic distribution of quartz enantiomorphs

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ABSTRACT

A statistically based re-evaluation of the evidence for a racemic abundance of quartz enantiomers suggests that, while this hypothesis is valid at the global scale, local deviations occur such that at any given location either $l$- or $d$-quartz may predominate. Thus, the hypothesis that the homochirality of life may have come about through interactions with a dominant quartz enantiomer at a particular location cannot be discounted.

Keywords: Enantiomorphic, quartz, homochirality, statistics

INTRODUCTION

Quartz ($\text{SiO}_2$), the most abundant silica mineral on the surface of Earth, is an enantiomorphic mineral because it can exist as $l$- (left) and $d$-quartz (right) single crystals and fibers. The morphological enantiomorphism of quartz derives from its structure, in which interconnected silicate tetrahedra ($\text{SiO}_4$), the building blocks of quartz, spiral in a clockwise direction in left-handed quartz (see Fig. 1) and counterclockwise in its right-handed counterpart. The $\alpha$-quartz thus crystallizes in either space group $P3_121$ or $P3_221$.

Origins of life hypotheses have sometimes invoked quartz as a plausible prebiotic inorganic substrate that might have jump-started the homochirality of life, by either breaking the symmetry of the initial racemic organic biomolecules or by amplifying small enantiomeric excesses. There have been numerous reports on the symmetry breaking properties of enantiomorphic quartz in catalytic syntheses of enantioenriched organic mixtures as well as in the enantioselective separation of amino acid enantiomers (Bonner et al. 1974, 1975; Bonner and Kavasmaneck 1976; Furryama et al. 1978, 1982; Hazen 2006; Kavasmaneck and Bonner 1977; Soai et al. 1999; Wedyan and Preston 2005). Therefore, the debate centers on whether quartz enantiomorphs are equally abundant on the surface of the Earth. This has particular significance because an imbalance in their abundance might imply a possible symmetry breaking mechanism.

Early studies on the distribution of quartz suggested an equal proportion of $l$- and $d$-quartz (Evgenii and Wolfram 2000). Palache (Frondel 1962), on the contrary, reported an $l$-quartz percentage of 50.5% in a total of 16,807 samples. More recently Evgenii and Wolfram (2000) summarized and analyzed data on quartz distribution based on a wide range of results from different sources. They concluded that $l$- and $d$-quartz are equally abundant as inferred from the ratio of excess enantiomorphic quartz ($\%d-%l$ or $\%l-%d$) to the total number of samples in each data set. This ratio tended to zero for the two data sets analyzed, one where $l$-quartz was in excess of $d$-quartz and vice versa.

Many authors have pointed out that excesses of either quartz enantiomorph in a given location are most probably due to seeding effects (Evgenii and Wolfram 2000). However there appear to be some inaccuracies in the paper by the previous authors in that they reported the unweighted rather than the weighted averages of the sample sets they examined. We have recalculated the data and find that the weighted average percentages are 51.06% $l$-quartz and 50.4% $d$-quartz, respectively, for the $l$- and $d$-quartz dominated data sets reported in Table 1.

Table 2 presents detailed data on the distribution of $l$- and $d$-quartz in Samshvildo, Georgia of the former USSR (Lemmelin 1944). This data set correspond to 40 subsets, each one composed of 100 crystals, to give a total of 4000 crystals (Table 1; entry 9). Statistical analysis of the data shows that they follow a normal distribution as supported by the histogram, boxplot of the quartiles, and the normality plot (Fig. 2). The mean percentage of $l$-quartz is 50.88 ± 1.42 at the 95% confidence interval, suggesting an equal distribution of $l$- and $d$-quartz at this particular location. We have further examined these data using the “coin-flipping” procedure described below, and the probability data provides some indication of the variability of enantiomorph ratios in small data sets that leads us to emphasize the importance

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Figure 1. The $l$- and $d$- quartz enantiomorphs (left and right figures, respectively; Buschmann et al. 2000).