

## Chapter 1

### ASYMMETRIC ADSORPTION ON MINERALS

#### Abstract

Chapter 1 considers the possible relationships of earthly clays and other minerals to the origin of chirality in organic molecules. Attempts to establish experimental evidence of asymmetric adsorption on clays were unsuccessful, but the search for chirality did find naturally occurring enantiomorphous crystals like quartz. Asymmetric adsorption of organic molecules on quartz crystals such as separation of racemic mixtures, like Co or Cr complexes, alcohols and other compounds, allowed for the conclusion that quartz crystals can serve as possible sources of chirality but not of homochirality. This latter conclusion results from the finding that all studied locations of quartz crystals contain equal amounts of *d*- and *l*-forms. The preparations of synthetic adsorbents such as imprinting silica gels are also considered. More than 130 references are analyzed.

#### 1.1. Introduction

There are many natural minerals and salts that possess optical activity in their crystalline state owing to their chiral lattices, such as quartz, cinnabar, mica, chlorates, bromates, and iodates. Crystal chirality of other minerals, like aluminosilicates, such as zeolites, were not investigated, but these minerals are considered by many investigators as possible sources of chirality and the origin of homochirality in our biosphere<sup>1,2,3</sup>. The optical activities of clays have not revealed reliable evidence of chirality<sup>4</sup> and therefore they do not play any positive role in our understanding of the origin or of the amplification of homochirality in nature.

On the other hand, if aluminosilicates are used as supports for chiral metal complex catalysts, they might reveal a contribution to asymmetric action as was found in the case of the hydrogenation catalyst [CoSalen] complex supported on hectorite<sup>5</sup>.

Even though clays have no chirality associated with their crystal structure, Julg and other authors<sup>6,7,8,9,10</sup>, claim asymmetric effects. As stated by Julg<sup>10</sup>: "...owing to the weak interactions, the two enantiomeric forms of kaolinite exhibit different energies. Experiments on synthesis and the

condensation of L-amino acids is a supplemental argument for the role played by kaolinite on the appearance of the first proteins and their L-homochirality...”.

## **1.2. Attempts of asymmetric adsorption on clays**

The role of clays in chemical evolution was suggested by Bernal <sup>1</sup> in 1951 based on preferential adsorption of optical isomers of amino acids by optically active crystals of quartz and possibly also by clays. Cairns-Smith <sup>2</sup> suggested that the surfaces of minerals, probably clays, played important roles in biogenesis. Field and Spencer <sup>11</sup> showed that in the presence of alumina the formation of glycine from water, CO<sub>2</sub>, and NH<sub>3</sub>; fructose from water and CO; and other sugars from HCHO and hydrogen, can be accomplished. Gabel and Ponnampereuma <sup>12</sup> may have confirmed these data in studies of the condensation of HCHO on alumina. According to Bernal's suggestion, <sup>1</sup> such processes provide the mechanism for the concentration of homochirality in nature. See also other authors positions on this subject <sup>13,14,15</sup>.

The first results on selective adsorption of individual enantiomers by clay minerals were claimed by Degens <sup>6</sup> and Jackson <sup>16</sup>. Degens <sup>6</sup> found 25% conversion of the polymerization of L-Asp after heating on kaolinite for 32 days but only 3% conversion of the polymerization of D-Asp and 14% of DL-Asp. These data are considered to result from the chiral character of the kaolinite surface favoring a chiral condensate made of L-Asp. Large changes in the extent of copolymerization on clays at shorter reaction times were found by Jackson <sup>16</sup>. He found a 25% preferential adsorption of L-phenylalanine (Phe) compared to D-Phe at pH 5.8. But both of these results are very doubtful because of experimental uncertainties. Nevertheless, based on the ideas of Cairns-Smith <sup>2</sup> and Degens <sup>6</sup>, theories of the origin of homochirality based on adsorption on chiral minerals were elaborated.

Degens <sup>6</sup> proposed that the surface of kaolinite contains centers which adsorbed mainly L-amino acids. In contrast, Bonner and colleagues <sup>17,18,19</sup> found that kaolinite is not an active chiral promoter neither in adsorption of enantiomers of Phe, nor in stereoselective polymerization of Asp. Flores and Bonner <sup>19</sup> incubated enantiomers of amino acids with kaolinite for 8 days but with negative results for stereoselective reactions. McCullough and Lemmon <sup>20</sup> tried to confirm those results <sup>6</sup> by using labeled aspartic acid (Asp) enantiomers and paper chromatography analysis for polymer formation, but they obtained only negative results. Jackson, <sup>21</sup> based on earlier data of Thomson and Tsukashina <sup>22</sup>, criticized the data of Bonner and coworkers <sup>17,18,19</sup> claiming that their negative results may be caused by uncertainties in different experiments and by traces of promoters of the process. Bondy and Harrington <sup>7,23</sup> emphasized the need to distinguish the adsorption of "natural" and "unnatural" enantiomers on clays. They studied diluted solutions of D-

and L-<sup>3</sup>H-labeled leucine (Leu), Asp, and glucose contacted with colloidal clay, bentonite and montmorillonite, and observed the radioactivity of samples bounded by the clay. They claimed that "natural" compounds are bound for 6.5-11.3 times more effectively than "unnatural" enantiomers: D-Leu, D-Asp, and L-glucose do not exhibit any selective adsorption on bentonite. They connected these data with the origin of chirality on Earth because the primordial clays can be disposed of once there exists more effective stereoselective samples, which possess chiral crystal structures. This difference could account for life forms possessing a great preponderance of L-amino acids and D-glucose. But Jackson et al.<sup>21</sup> objected to the possible chirality of the clays used and the validity of experimental data in these experiments. Wellner<sup>4</sup> indicated that the chiral structure of bentonite is not confirmed yet and the differences of adsorption of optical isomers could not be responsible for differential binding. Moreover it is necessary to note that the bentonite structure differs from that of kaolinite. Friebele and colleagues<sup>24</sup> carefully treated a sample of montmorillonite and studied its adsorption of enantiomers of Val, NorVal, and *alpha*-aminobutyric acid. They found that at pH 10 the difference in the excess of adsorption of L-amino acids is equal to 0.5-2.0 %. Their standard deviation of gas chromatographic (GLC) analysis was 0.01%, which was much better than that claimed earlier by Bonner and colleagues (0.2%)<sup>25</sup>. In conclusion, Friebele and colleagues<sup>24</sup> noted that "...clay minerals have no known chirality; therefore, to rationalize a small asymmetric effects due to adsorption of amino acid is difficult, but a very small effect can not be excluded...". Later authors<sup>26</sup> rejected the idea of asymmetric adsorption on clays. Yuatt and Brown<sup>27</sup> showed that stereoselective binding of amino acids by clays does not occur and the earlier results can be attributed to adsorption of the radiochemical decomposition products formed during the experiments<sup>7,23</sup>. Therefore, it will be more correct to measure the adsorption by the amount of adsorbate on the surface of the adsorbents rather than by the decrease in the concentration of the substrate in solution. This criticism belongs to Bonner's experiments too, where he<sup>28,29</sup> announced differential adsorption of up to 12-20 %. Friebele and colleagues<sup>24</sup>, using GLC methods, seemed to show that there is stereoselective adsorption of enantiomers of amino acids on Na-montmorillonite in solution at pH 3, 7, and 10. L-amino acids were 0.5-2.0% more adsorbed in the clay than were their D-enantiomers. But later it was noted that the first results were erroneous and it was shown, using enantiomeric analysis of the same samples, that the results were not consistent in all cases with the GLC data (data in Table 1.1 with asterix) and no differential adsorption was found. Thus these results show that apparently clays have no significant ability to sort out L- and D-amino acids under the conditions studied and that clays have not played an important role in the enantiomeric selection of amino acids in the processes of chemical evolution.

Amino acids	pH of solutions		
	3	7	10
Alanine	1.022	0.976	0.935
		1.001*	0.983*
$\alpha$ -Aminobutyric acid	1.005	0.996	0.925
NorValine	0.986	0.979	0.986
Valine	0.977	0.996	1.015

\* Determined using amino acid analyzer.

Adapted modified data from Friebele et al.<sup>24</sup>

**Table 1.1.** Ratio of *D/L* of amino acids adsorbed on Na-Montmorillonite as determined by GLC<sup>24</sup>.

Ignoring all these negative experimental data Julg<sup>8,9,10</sup> calculated, using a "self consistent molecular method", that the adsorption energy of L-amino acids on one of the "chiral" forms of kaolinite is 0.03-0.19 kcal/mol greater than that for the D-enantiomer, and this differential adsorption can be the basis for spreading L-amino acids in nature. Moreover, he postulated<sup>9</sup> that addition of CN<sup>-</sup> to ethyliminium cation on the surface of kaolinite can form a precursor of chiral L-Ala that is favored over the corresponding D-precursor by 0.36 kcal/mol. This mechanism can explain the preponderance of L-amino acids rather than D-amino acids. Furthermore, due to weak interactions assumed for the calculations<sup>10</sup>, the enantiomeric forms of kaolinite leading to the formation of L-amino acids are more abundant than those leading to the D-enantiomer. But after Bonner<sup>28,29</sup>, Julg's speculations<sup>8,9,10</sup> have no experimental evidences and are fully contradicted by recent experimental data. Thus at the present time, the main conclusion must be drawn that clays do not reveal any asymmetric adsorption and can not serve as sources of chirality in nature.

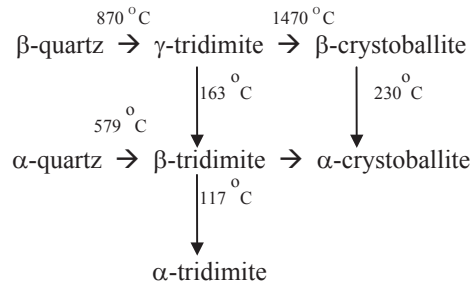
### 1.3. Asymmetric adsorption on quartz crystals

#### 1.3.1. Properties and morphology of quartz crystals

There are seven crystal modifications of natural quartz: *alpha*- and *beta*-quartz; *alpha*-, *beta*-, and *gamma*-tridimite; and *alpha*- and *beta*-cristoballite. Below in Scheme 1.1. are shown the temperatures of transfers between the different quartz modifications.

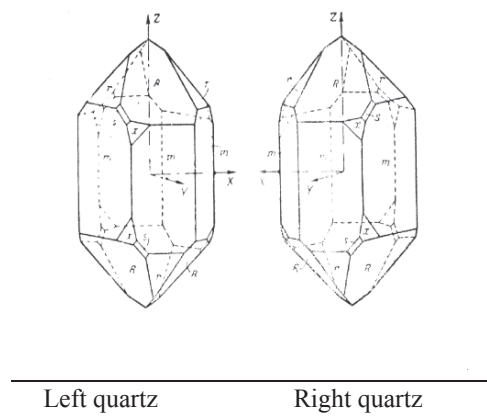
At the conversion point (579 °C) optical rotation reveals a sharp jump of 4.5%. The value and sign of optical rotation of the quartz crystal depends on the direction of the beam of polarizing light passing through the crystal. If  $\phi$  is the angle between the direction of the beam of light and the optical axis of the crystal (Fig. 1.1.) and  $[\alpha]_{90}$  the specific optical rotation in the direction

perpendicular to the optical axis, then the specific optical rotation at a given  $\phi$  in the range  $0^\circ - 90^\circ$  can be calculated by  $[\alpha] = [\alpha] \cos \phi + [\alpha]_{90} \sin \phi$ .



**Scheme 1.1.**

Measurement of the (-) rotation ( $\alpha_{90}$ ) in *d*-quartz ( $\alpha_0$ ) has definite difficulties because of double refraction. That is why the (+)-rotation only is usually accepted for *d*-quartz.



**Figure 1.1.** Morphology of quartz crystals (according to Cedy<sup>33</sup>).

The habits of an ideal quartz crystal (Fig.1.1.) has five simple forms: rhombohedrons, R, and trapezohedron, x, hexagonal, prism, and bipyramidal. The crystal has its main optical vertical axis of third-order and three horizontal axes of second-order directed to ribs of the prism. These axes are so called "electric ones". Examination of the positions of the faces of a crystal reveals the sign of its optical rotation. The crystal is a *d*-quartz if x and s faces are situated at the top of the face of the right side prism. The crystal is an *l*-quartz

if the *x* and *s* faces are situated on the top of face at left (Fig. 1.1.). However, in nature, findings of optically pure crystals are rather rare. Mostly, crystals form twins. For example, inside individual quartz crystals may be areas of (+)- and (-)-rotating quartz, called "Brazilian twins", that differ in their sign of rotation. Other areas of quartz crystals may exhibit one sign of rotation, (+) or (-), but are oriented to each other in such a way that their electric axes are directed opposite to each other. These are called "Douphine twins". Both types of twins do not exhibit piezoelectric properties. On the other hand, pure, rather rare quartz crystals are optically and electrically active.

The optical activities of quartz crystals are caused by structural arrangements of Si and O atoms situated along helix axes in the crystal lattice. A right helix structure corresponds to a (+)-optical rotating quartz and a left helix to a (-)-rotating quartz<sup>30,31,32</sup>.

Selection of optically pure crystals can be accomplished with the aid of a polariscope in which the thin plates of quartz are examined between crossed Nicol prisms in polarized light. These plates are sawed perpendicular to the optical axis of well formed natural crystals. Brazilian twins exhibiting bright interference patterns in crossed Nicol prisms must be broken out. Only optically pure areas are selected for further use, for example, for asymmetric adsorption and for asymmetric catalysis. Piezoquartz as plates of an oblique cut, called the "Cut of Curie", are used in radio electronics and can be identified by the sign of their optical rotation according to the method of Lemlein<sup>30,31,33</sup>. According to this method, the etched plate of piezoquartz is preliminarily examined for the absence of Brazilian twins under a beam of light placed close to the observer's eye and directed at an angle of 3-5° to the observer's eye. As a result of reflections of light from the ribs of the three vicinal facets of the pyramids the shape of the peculiar light picture reveals *d*- or *l*-quartz. The correct method of selection of optically pure quartz crystals is very important for experiments in which they are used and also the method is important for studying the origin of optical activity in the nature. At present there are several indications for equivalence or for prevalence of one of the morphological forms of quartz crystals over the surface of Earth<sup>34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44</sup>.

Mason<sup>34</sup> and Tranter<sup>35</sup> performed calculations and alleged that a 1.4% excess of *l*- over *d*-quartz on the surface of Earth is the inevitable consequence of a parity-violating energy difference (PVED). They calculated that the *l*-quartz is stabilized by 10<sup>-17</sup> kT per SiO<sub>2</sub> unit<sup>35-37</sup>. This allegation is based on a report<sup>40</sup> that there is 50.17% *l*-quartz and 49.3% *d*-quartz in 16,807 samples collected worldwide; that is an excess of 1.4% of *l*-quartz. But a more recent survey of 27,053 samples<sup>38,39</sup> yields 50.17% *d*-quartz and 49.83% *l*-quartz, which is a 0.39% excess of *d*-quartz. Therefore it is necessary to accept the fact that the terrestrial distribution of optically active quartz crystals is quite random and, consequently, no basis exists for calcula-

tion of PVED for quartz crystals<sup>35-37</sup>. Nevertheless, the quartz crystals and other minerals, for example, clays (see Chapter 1.2) are considered as possible sources of asymmetry in nature<sup>1, 8-10,45,46</sup>.

### 1.3.2. Asymmetric adsorption on quartz crystals

Unlike the clays, owing to its chiral lattice, quartz must display certain selectivities for the adsorption of mainly neutral organic compounds possessing molecular or crystal-like chirality. Glucose, galactose and arabinose selectively adsorb on quartz crystals and quartz dissolves in solutions of these monosaccharides<sup>47</sup>. Racemic acids seem not to be resolved on quartz<sup>48</sup>; however, it has been shown that *d*- or *l*-quartz exert an orienting influence on the epitaxy of hemihedral crystals of Glu, Ala, and Gly. For example, the influence is seen for Glu, Ala, and Gly adsorbed on the surface of *l*-quartz crystals {1010}, and of Ala on *l*-quartz {1011}. These crystals are like the asymmetric epitaxy of crystals of (+) camphor on biotite and calcite<sup>49</sup>.

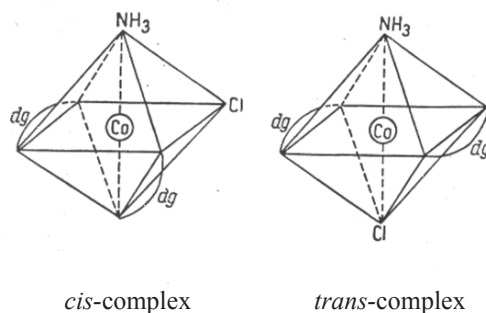
In general, asymmetric adsorption on quartz crystals can not be effective. Selective adsorption of enantiomers or attempts for resolution of racemates have not shown positive results. Thus, attempts to resolve racemic *p*-phenylenebisiminocamphor,  $\beta$ -naphthylazomandelic acid, and the racemic free radical, phenyl-biphenyl- $\alpha$ -naphthylmethyl, have been unsuccessful<sup>50</sup>. Klabunovskii and Patrikeev<sup>51</sup> partially resolved racemic 2-butanol using a chromatographic technique based on counter current action. In a glass column vapors of racemic 2-butanol passed upward against a falling quartz powder. In this process, *l*-quartz preferentially adsorbed (+)-butanol. Then the butanol with a small excess of the (+)-enantiomer was removed from the quartz by heating in a desorbing zone. Both the (+)-enriched butanol and the quartz powder were recycled back into the process. After thirty cycles the (+)-2-butanol was recovered with an ee 0.22%<sup>51</sup>.

Asymmetric adsorption on quartz powder was also shown by measurements of the adsorption capacity of *d*- and *l*-quartz in relation to (*S*)-(-)-2-methylbutan-1-ol (that is, the commercial (-)-amyl alcohol, AmOH, consisting of 75% (-)-alcohol in a mixture with 3-methylbutan-1-ol) adsorbed on samples of *d*- and *l*-quartz with equal surface areas, and the decrease in optical rotation was measured after adsorption<sup>51</sup>. It was found that *d*-quartz adsorbed more (-)-AmOH by 2.3% than *l*-quartz. Taking into account the 1 m<sup>2</sup> surface areas of the quartz samples, this 2.3% amounts to 0.06% (-)-AmOH more than *l*-quartz. In contrast, it is also necessary to note that Ohara et al.<sup>52</sup> tried in vain to resolve 2-butanol on optically active quartz.

The selective adsorption of enantiomers of transition metal complexes on quartz proved to be more successful. For the first time, in 1935, Tsuchida and colleagues<sup>53</sup> reported the partial resolution of several racemic Cr- and Co-complexes using chromatographic adsorption on columns composed of *d*- or *l*-quartz crystals originating from Kimbusen and Naegi deposits. The steric

configuration of chlorobisdimethylglyoximoamine-Cobalt has not been determined. However, a solution of this complex over *l*-quartz gave a (+)-rotation and over *d*-quartz a (-)-rotation ( $0.02 \pm 0.05^\circ$  in a 4 cm polarimeter tube).

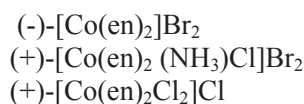
Resolution of a complex even to a very small extent could demonstrate that the original complex was a racemic mixture. Thus, complexes like  $[\text{Co}(\text{dimethylglyoximo})_2(\text{NH}_3)\text{Cl}]$  were partly resolved on quartz powder. The spatial configuration of this complex was unknown. From the theoretical point of view it was expected that only the *cis*-form of the complex should exhibit optical activity. In agreement with this expectation, resolution of the tris(dimethylglyoximo)cobaltate(III) complex on quartz exhibited a poor but definite optical activity revealing the configuration of the complex to be *cis* rather than *trans*<sup>53</sup>.



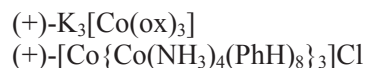
**Scheme 1.2.** Structures of *cis*- and *trans*- $\text{Co}(\text{dimethylglyoximo})_2(\text{NH}_3)\text{Cl}$  complexes (according to Klabunovskii<sup>32b</sup>).

Therefore it was sufficient to resolve this complex into enantiomers to determine its spatial structure. This complex does not form diastereomers and the only method of its resolution was asymmetric adsorption on crystals of quartz – a very inert material. In this manner, a solution of samples of the complex was vigorously shaken with quartz powder, the solution was filtered and its optical rotation measured. On *l*-quartz the optical rotation of the remaining solutions reached from  $+0.05^\circ$  to  $+0.075^\circ$  and on *d*-quartz they reached from  $-0.075^\circ$  to  $-0.13^\circ$ . Thus the configuration of the complex proved to correspond to the *cis*-structure. The *d*-quartz preferentially adsorbs the (+)-complex and the *l*-quartz the (-)-complex. Brazilian twin quartz gave negative results.

Using the same method, Tsuchida et al.<sup>53,54</sup> found that the *d*-quartz preferentially adsorbs enantiomers of the following complexes:







In 1938 Karagunis and Coumoulos<sup>55</sup> suggested such an effect on the resolution of racemic Cr-, Co-, and Pt-complexes and noted that "...resolution on optically asymmetric surfaces of minerals might have been the genesis of the first optically active organic molecules in Nature."

Ikeda<sup>56</sup> found that *d*-quartz can partially resolve (1,2,3,4-tetrahydronaphthyl)hydroperoxide and cyclohexylhydroperoxide with specific rotations of +20.0° and -18.5°. As the author indicated "...method of course is not quantitative one but can be used for decision of question is given compound racemic one or not...".

Kuebler and Bailar<sup>57</sup> studied the resolution on quartz powder (140-200 mesh) of the racemic complex: potassium dinitro(*N*-methyl-*N*-ethylglycinate)platinum. Resolution proved to be somewhat better than on crystals of quinine bisulfate. For example, a solution of the complex was shaken with quartz powder and after filtration was examined polarimetrically. Typically, optical rotations diminished with time and in 5-7 hrs fell to zero. On *l*-quartz rotations were +0.028°, and on *d*-quartz -0.024°.

Also complexes [NaCo(en)(Ac)<sub>4</sub>] (**I**) and [BaCo(en)(Ac)<sub>4</sub>]Br (**II**) were partially resolved on *d*-quartz powder<sup>58</sup>. Optical rotations for **I** on *d*-quartz were between -0.063° and -0.012° ± 0.003-0.007°, and for **II** on *d*-quartz, -0.018°. The (+)-rotating forms of both complexes preferentially adsorbed on *d*-quartz.

The complex *N,N'*-bis(salicylidene-trimethylene-tetrammino)cobalt was partially resolved on *d*-quartz with a rotation of -0.03° (specific rotation -300°)<sup>59</sup>.

<u>Complex</u>	<u>Maximum optical rotation</u>	
	<u>(-)-rotation</u>	<u>(+)-rotation</u>
K <sub>3</sub> [Cr(ox) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ]	0.70	0.60
K <sub>3</sub> [Co(ox) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ]	0.50	0.30
K[Cr(ox) <sub>2</sub> (en)]	0.17	0.20
[Co(ox)(en) <sub>2</sub> (H <sub>2</sub> O)]Cl	0.35	0.20
[Co(en) <sub>3</sub> ]Cl <sub>3</sub>	1.0	0.15
[Co(dg) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Cl	0.80	1.00

ox = oxalate; en = ethylenediamine; dg = dimethylglyoxime

**Table 1.2.** The maximum optical rotation values of fractions of chromatographic resolution of racemic complexes with a quartz powder column (modified data adapted from Schweizer et al.<sup>60</sup>).

Karagunis and Coumoulos<sup>55</sup> tried to resolve the racemic [Cr(en)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>1/2</sub>]Cl<sub>3</sub> complex on quartz by the chromatographic method. Through a vertical column packed with activated (heating in vacuum) quartz powder was passed

a solution of the complex in 85% ethanol. In the case of *d*-quartz the first fractions of eluent had a rotation of  $+0.023^\circ$  followed by fractions with a rotation of  $-0.05^\circ$ . On *l*-quartz the opposite picture was observed; the first fractions had a rotation of  $-0.058^\circ$  followed by fractions with rotations of  $+0.054^\circ$ .

Using the same method Schweizer and Talbott<sup>60</sup> found selective adsorption on *l*-quartz with a specific area of  $4 \text{ m}^2/\text{g}$  in resolution of several racemic Co and Cr complexes, such as  $\text{K}_2[\text{Cr}(\text{ox})_2]$  and  $\text{K}_2[\text{Co}(\text{ox})_2]$ . The 0.01M solutions of the complexes were passed through a column of quartz powder (300 mesh). The eluate was divided into 20 fractions, among which fractions 6 through 10 exhibited progressive changes of sign of rotation. In Table 1.2. is shown the maximum optical rotations of the fractions. More effective resolution was observed when the isolated fractions were passed through a second and third column. Results received in resolution of the racemic complex  $\text{K}_3[\text{Cr}(\text{ox})_3(\text{H}_2\text{O})]$  are shown on Table 1.3.

No. of fractions	optical rotation	No. of fractions	optical rotation
1	- 0.90	6	- 1.30
2	- 1.00	7	- 1.20
3	- 1.20	8	- 0.45
4	-1.30	9	+ 0.05
5	- 1.10		

**Table 1.3.** Optical rotations of fractions in resolution of racemic Cr-complex on quartz (Klabunovskii<sup>1b</sup>).

From the thin-layer technique, Kamai and colleagues<sup>61</sup> found partial resolution of racemic  $[(\text{Bz})(\text{Et})(\text{pentyl})(\text{Ph})\text{As}]\text{Br}$  on vibro-crushed *d*-quartz powder: the (-)-enantiomer adsorbed preferably. Chernyaev and coworkers<sup>62</sup> obtained partial resolution of the racemic complex  $[\text{Pt}(\text{Hal})(\text{NH}_3)\text{NO}_2]$ . On *l*-quartz the (+)-complex was adsorbed preferentially and exhibited only (+)  $0.02\text{-}0.05^\circ$  at 579 nm, even so, this rotation proved to be enough for identification of the spatial structure of the complex.

Using *d*-quartz partial resolution was observed for the acetylacetonate chelates  $[\text{Cr}(\text{acac})_3]$  and  $[\text{Co}(\text{acac})_3]$ , in which the (-)-complex was preferentially adsorbed<sup>63</sup>. Sievers and coworkers<sup>64</sup> found the partial gas chromatographic resolution of racemic  $[\text{Cr}(\text{F}_6\text{acac})]$  on *d*-quartz at  $56^\circ\text{C}$ , in which the first fraction had a specific rotation of  $260^\circ$ .

By shaking *d*-quartz powder with solutions of the racemic complex  $[\text{Be}(\text{PhCOCH}_2)_2\text{C}=\text{O}]_2$  Bush and Bailar<sup>65</sup> obtained very small rotations of  $+0.011$  and  $+0.026^\circ \pm 0.003^\circ$ , but these were enough for evidence of tetrahedral coordination of Be in the complex.

It is well known that silica plays an important role in living matter. This was shown by the selective adsorption of some sugars on quartz crystals<sup>66</sup>. Consequently, Schwab and Wahl<sup>67</sup> tried to determine the asymmetric adsorption of silicic acid specimens recovered from the mushroom *Euspongia* and from the Japanese sponge. However, they did not find any asymmetric adsorption. It turned out that the structure of this silicic acid is similar to the structure of silica. It possesses no helical structure and cannot play any role in the formation of optically active compounds in organisms.

Amariglio et al.<sup>68,69,70,71</sup> failed to reproduce the results of Tsuchida and coworkers (1936) and Klabunovskii and coworkers (1951) on adsorption (and catalysis) over quartz crystals. She concluded that all former results were erroneous because of the small optical rotations of the substrates to be resolved. Such small rotations were of the size which might be obtained from the slight solubility of optical active quartz, and when combined with the experimental errors in the polarimetric measurements, these could account for the very small rotations observed from the adsorbates. But analysis of her reports<sup>68-71</sup> showed that critical examination was incorrectly carried out. For example, the samples of quartz in her experiments<sup>68-71</sup> were not well identified, and suspension of *d*- and *l*-quartz and even of glass pyrex powder gave the small optical rotation with the same sign ( $-0.05^\circ$ ) independent of the sign of the quartz used. Therefore, the negative results<sup>68-71</sup> cannot be considered valid. The same conclusion is reached with regards to catalysis using "quartz-catalysts"<sup>66-69</sup>.

Based on the tentative and shallow negative results received by Amariglio and coworkers<sup>66-69</sup>, Bonner<sup>72,73,74,75</sup> at first came to the tentative conclusion that "...the phenomena of asymmetric adsorption on quartz crystals as asymmetric adsorbate is open to question...". Later, Bonner and colleagues<sup>72-75</sup> tried to verify the asymmetric adsorption on quartz using a radiochemical method with labeled amino acids as substrates. This is a more precise technique than the polarimetric technique and revealed an excess of adsorption of one enantiomer of one of the amino acids as high as 20 %.

In the radioactive tracer experiments <sup>3</sup>H- or <sup>14</sup>C-labeled *D*- or *L*-Alanine hydrochloride (Ala HCl) in DMF solutions were equilibrated with finely powdered *d*- or *l*-quartz<sup>72,73</sup>. Differences in rates of radioactive disintegrations of solutions before and after equilibration gave a measure of the amount of Ala HCl adsorbed on the quartz samples. In general, *d*-quartz preferentially adsorbed *D*-Ala HCl and the *l*-quartz *L*-Ala HCl to the extents of 1-1.8%. These experiments used finely powdered samples of *d*- and *l*-quartz which had been prepared from known morphological handedness and optical rotation, but the authors failed to mention how the Brazilian twins (if any) were removed from quartz samples<sup>72,73</sup>. They did note<sup>73</sup> that samples of quartz were prepared by hydrothermal growth and that crystals were checked

for uniform optical handedness as well as for enantiomerism by measurements of optical rotations at 589 nm. The crystals prepared had specific rotations of +21.2° and -26.724° for 1 mm plates (somewhat more than found for natural quartz). Table 1.4. summarizes results derived from the radioactive labeling experiments.

<u>Adsorbate</u>	<u>% adsorbed by <i>l</i>-quartz</u>	<u>% adsorbed by <i>d</i>-quartz</u>	<u>Differential adsorption, %<sup>a</sup></u>
<i>L</i> - <sup>3</sup> H-Ala HCl	29.35	28.33	1.02
<i>L</i> - <sup>3</sup> H-Ala HCl	28.35	26.68	1.75
<i>L</i> - <sup>3</sup> H-Ala HCl	22.21	21.03	1.18
<i>D</i> - <sup>14</sup> C-Ala HCl	29.00	39.38	-1.30
<i>D</i> - <sup>14</sup> C-Ala HCl	25.92	26.88	-0.96

<sup>a</sup> percent adsorbed by *l*-quartz minus percent adsorbed by *d*-quartz.

**Table 1.4.** Adsorption of <sup>3</sup>H- and <sup>14</sup>C-labeled *D*- and *L*-alanine hydrochloride on *d*- and *l*-quartz crystals (modified data adapted from Bonner et al. <sup>72,73</sup>).

Table 1.4. shows that the differential adsorption of *L*-Ala on *l*-quartz and of *D*-Ala on *d*-quartz was as much as 1.0-1.8%. Interestingly, results received by the same author on the asymmetric adsorption of racemic *DL*-Ala HCl <sup>74</sup> in which only one of the enantiomers (*D*- or *L*-Ala ) was labeled with <sup>3</sup>H or <sup>14</sup>C showed differential adsorptions as high as 20% (Table 1.5).

	<u>Labeled Enantiomer of DL-Alanine</u>		
	<u><i>L</i></u>	<u><i>L</i></u>	<u><i>D</i></u>
% adsorbed by <i>l</i> -quartz	60.0	60.1	44.1
% adsorbed by <i>d</i> -quartz	40.0	39.9	55.9
Differential adsorption, %	20.0	20.2	11.8

**Table 1.5.** Differential adsorption of labeled *D*-enantiomer in *DL*-alanine on *d*-quartz (modified data adapted from Bonner et al. <sup>74</sup>).

These data in Table 1.5. show that the adsorption of one of the enantiomers from a racemate greatly exceeds its adsorption when alone. Of course one must neglect the possibility that during adsorption the two enantiomers exchange the label, which can distort the results.

To study the effect of the functional groups in Ala on its adsorption on the quartz surface, several derivatives were prepared. For example Ala HCl was esterified with isopropyl alcohol (Ala-*i*Pr ester) and acetylated with F<sub>3</sub>CCOCl. The results of such studies indicated that adsorption of Ala HCl is mainly attributable to the interaction of the NH<sub>3</sub><sup>+</sup> group with the quartz surface.

Adsorption of <sup>3</sup>H-labeled Ala-*i*Pr ester on *d*- and *l*-quartz was studied using gas chromatography (GLC). Adsorption of this ester proceeds from

chloroform solution followed by its desorption by chloroform or methanol. It was found that *l*-quartz preferentially adsorbs the *D*-enantiomer. Essential symmetric data were obtained when the adsorption-desorption process was repeated with *d*-quartz. The main results are summarized in Table 1.6.

Adsorbate	Percent Desorption from	
	<i>l</i> -Quartz	<i>d</i> -Quartz
<i>D</i> -Ala-i-Pr	43.8	52.4
<i>L</i> -Ala-i-Pr	56.2	47.6
%ee (% <i>D</i> -% <i>L</i> ) <sup>a</sup>	-12.4	+4.8

<sup>a</sup> ee = enantiomeric excess ( $D-L/D+L$ )

**Table 1.6.** Asymmetric adsorption-desorption of <sup>3</sup>H-*DL*-Ala-iPr ester on *l*- and *d*-quartz, measured by GLC (modified data adapted from Kavasmaneck et al. <sup>75</sup>).

Using labeled *DL*-Ala HCl these results were confirmed <sup>74</sup> by obtaining a differential adsorption of 12-20% (percent adsorption on *d*-quartz minus percent adsorption on *l*-quartz). The adsorption of *D*- and *L*-Ala-iPrHCl in chloroform solution was studied using GLC <sup>75</sup>. In this case *d*-quartz preferentially adsorbed the *L*-Ala ester and *l*-quartz the *D*-Ala ester with enantiomeric enrichments of up to 1.5-12.4%. Such large differential enrichments are very doubtful and can indicate possible artifacts, although these data were confirmed later by Furoyama and coworkers <sup>76</sup> by stereoselective adsorption on quartz <sup>76,77</sup>. According to Furoyama and colleagues <sup>76</sup> racemic <sup>14</sup>C-alanine from ethanol at 8°C was partly resolved on *d*- and *l*-quartz powder with a specific area of 0.08 sq.m./g (purchased from Toyo Communication Co.) with preferential adsorption of *L*-Ala on *l*-quartz.

Thus, these data also confirmed the earlier findings of Tsuchida <sup>53</sup> and Karagunis <sup>55</sup>. The positive results in asymmetric adsorption of amino acids, as shown in the work of Bonner and coworkers <sup>72-75</sup>, "...required carefully contrived and rigorously maintained anhydrous conditions, with mere traces of moisture nullifying the effect..."

Attempts were unsuccessful in resolving several organic and inorganic racemates {Cr and Co acetylacetonates, lipoic acid (1,2-ditolan-3-valeric acid) and penicillamine (3-mercaptopvaline) and tartaric acid} on chiral inorganic enantiomorphic crystals <sup>78</sup> other than quartz, such as cinnabar <sup>79</sup> NaClO<sub>3</sub>, NaBrO<sub>3</sub>, NaIO<sub>3</sub>, NiSO<sub>4</sub>•6H<sub>2</sub>O, sodium uranyl acetate, and benzil <sup>80</sup>.

Sodium chlorate, NaClO<sub>3</sub> gives well formed crystals possessing optical activity. Its absolute configuration was investigated by means of optical rotatory dispersion (ORD). The dependence of specific rotation,  $[\alpha]$ , of a crystal of NaClO<sub>3</sub> with wave length,  $L$ , in nm in the range 237.6-875 nm can be given by <sup>81</sup>:

$$[\alpha] = 1.2387 \text{ L}^2 / (\text{L}^2 - 0.0081)^2$$

Ferroni and Cini <sup>82</sup> tried to resolve the racemic chelate complex  $\text{Be}[(\text{PhCOCH})_2\text{CO}]_2$  using optically active crystals of  $\text{NaClO}_3$  as chiral adsorbents, but results were uncertain (see Table 1.7.).

Sample of $\text{NaClO}_3$	Observed rotation of resolved complex <sup>a</sup>
<i>d</i> - (right rotation )	+ 0.067°
<i>l</i> - (left rotation )	0.00°
Racemate crystals with an excess of <i>d</i> -crystals (from Merck)	+ 0.071°
Racemate (50% <i>d</i> -crystals + 50% <i>l</i> -crystals)	+ 0.017°

<sup>a</sup>  $\alpha_{436}$  of Be-complex

**Table 1.7.** Resolution of racemic beryllium complex on sodium chlorate crystals (modified data adapted from Ferroni et al. <sup>82</sup>).

In addition by Gillard (1979) it was noted that all resolution data on crystals which owe their chirality to crystal packing rather than to molecular chirality are very doubtful based on his own results showing the optical rotation of suspension of *l*- $\text{NaBrO}_3$  in benzene exhibit rotations comparable with those found previously <sup>80</sup>.

Thus, optically active quartz crystals remain the only relatively effective stereoselective inorganic adsorbent and this fact must be used in discussions of the role of asymmetric adsorption on quartz crystals in the origin (or amplification) of optical activity on the surface of the Earth (see Bernal <sup>1</sup> and <sup>28,29,83,84,85</sup>).

#### 1.4. Imprinting chiral adsorbents: specifically modified silica gels

Molecular recognition is one of the main phenomena of living matter. In enzymes recognition is the basis of the well-known "Lock-and-key" mechanism first discussed by E. Fischer. The generation of sites in inorganic materials with the ability of chiral recognition is of particular interest because such solids can be used for molecular separation including enantiomeric enrichments by adsorption and by chiral catalysis. The target to create complementary cavities in inorganic materials using molecular imprinting with a removable template is of theoretical and practical interest.

Polyakov was first to create complementary cavities on the surface of silica gel <sup>86,87</sup>. He removed water from silica gel in atmospheres of benzene, toluene, or xylene vapors and found that the pore structure of the resulting silica gel is influenced by the size and shape of the imprinting molecules in the gaseous atmosphere. Such silica gel dried in a benzene atmosphere

adsorbed benzene well but toluene and xylene poorly. In such an environment, the adsorbate produced a matrix with the size and shape suitable for its adsorption. Objections that the structure of the silica gel still retains traces of the template compounds were removed by Dickey<sup>88,89</sup>, who achieved the idea of Pauling<sup>90,91</sup> of imprinting of molecules or "molecular memory" using the adsorption of alkyl-oranges on silica gels formed in the presence of the same adsorbates. As shown below, adsorbents revealed strong specificity to that adsorbate which was originally formed with the same alkyl-orange:  $\text{HSO}_3\text{-C}_6\text{H}_4\text{-N=N-C}_6\text{H}_4\text{-NR}_2$ .

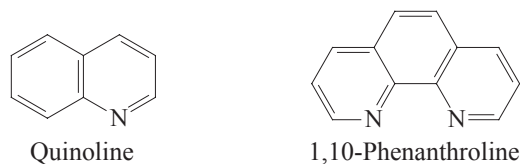
These data give very strong evidence of imprinting but they have poor reproducibility and were criticized<sup>92</sup>. Morrison et al. (1959) seemed to view the evidence as favoring an association mechanism in which the unextractable dye particles act as centers to attract their own kind more strongly than one of their homologues. Several positive examples were described later<sup>93,94,95,96</sup>

Erlenmeyer<sup>97,98,99</sup> and Haldeman and Emmett<sup>100</sup> confirmed the results of Dickey<sup>88,89</sup> and developed further possibilities of this method of preparation of specifically formed silicas.

Dye added to <u>silica gel</u>	<u>Silica Gel modified with</u>			
	<u>Methyl orange</u>	<u>Ethyl orange</u>	<u>Propyl orange</u>	<u>Butyl orange</u>
Methyl-orange (R = Me)	17(3.5)*	8(1.6)	3(1.1)	2(1.1)
Ethyl-orange (R = Et)	9(2.5)	30(9.0)	10(2.1)	3(2.2)
Propyl-orange (R = Pr)	7(2.3)	22(5.0)	30(20)	25(6.0)
Butyl-orange (R = Bu)	5(1.5)	13(2.8)	30(5.0)	30(15)

\*Numbers in parentheses are the ratio of the adsorption of the dye on the imprinted silica gel to its adsorption on the non-imprinted silica gel.

**Table 1.8.** Specific adsorption of dyes ( $\text{HSO}_3\text{-C}_6\text{H}_4\text{-N=N-C}_6\text{H}_4\text{-NR}_2$ ) on silica gels modified with these dyes; adsorption of Dye  $5 \times 10^{-5}$  mmol/kg adsorbent (modified data adapted from Dickey<sup>88,89</sup> and Davis<sup>97</sup>).



**Scheme 1.3.**

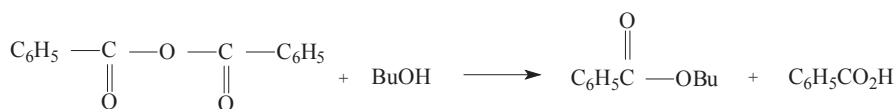
Erlenmeyer (1964) found that specifically prepared silica can preferentially adsorb compounds with analogous structures, for example, silica-Quinoline preferentially adsorbs 1,10-phenanthroline (Scheme 1.3.).

Waksmundzki and coworkers<sup>101,102</sup> and Bernhard<sup>103</sup> also received positive results. Patrikeev, Balandin, and colleagues<sup>104</sup> found that silica gel prepared in the presence of diketopiperazine catalysed the polycondensation of alanine esters into diketopiperazine faster than into tripeptide. Other examples of specific adsorption on silicas especially formed were given by Patrikeev and coworkers<sup>105,106,107</sup>.

Later, various aspects of the catalytic actions of specifically formed adsorbents as catalysts were discussed by Jencks<sup>108</sup>, who theorized that antibodies prepared in the presence of stable analogues that mimic transition states may be able to catalyze the corresponding reactions. Recently Lerner<sup>109</sup>, and Mosbach<sup>110</sup> used transition state analogues to imprint the formation of antibodies that were able to function as catalysts for reactions from which the transition-state analogues were prepared. Confirmation of these concepts was obtained from studies of the Claisen rearrangement of (-)-chorismate to form prephenate<sup>92,111</sup>.

Positive results were reported also by Morihara and colleagues<sup>112,113,114,115</sup> in a number of publications. Based on their experiments, the concept of "Footprint-catalysis" was developed. A silica gel surface was doped with Al<sup>3+</sup> and the chiral template molecule *N*-benzoyl (*N*-benzyloxycarbonyl-L-Alanine-amide). This embedded imprint molecule was removed by methanol extraction after aging and drying the silica gel<sup>114</sup>. The cavities thus formed displayed enantioselective catalysis for 2,4-dinitrophenolysis at 30°C in MeCN solution of the substrate benzoic *N*-benzyloxycarbonyl-L-Alanine anhydride. The observed maximal rates (10<sup>-2</sup> L mol<sup>-1</sup>) for "L-Silica", "DL-Silica", and control Silica (without imprinting) with L-substrate were 2.35, 1.31, and 0.81, respectively<sup>116</sup>, and indicated a definite acceleration for the system: L-Substrate-L-Silica.

Also, they imprinted an aluminated silica with the transition state analogue for the butanolysis of benzoic anhydride, removed the imprinting molecule by extraction to form cavities in the structure of the silica, and were able to catalyse the butanolysis (Scheme 1.4.).

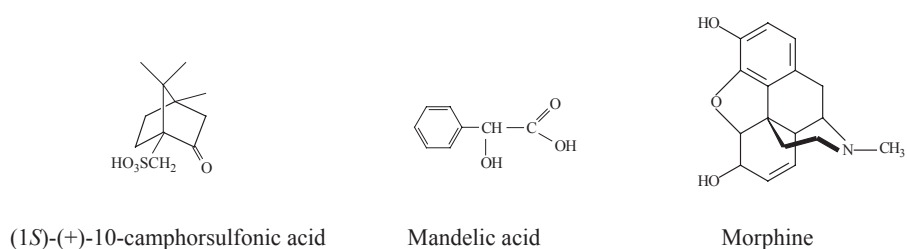


**Scheme 1.4.**

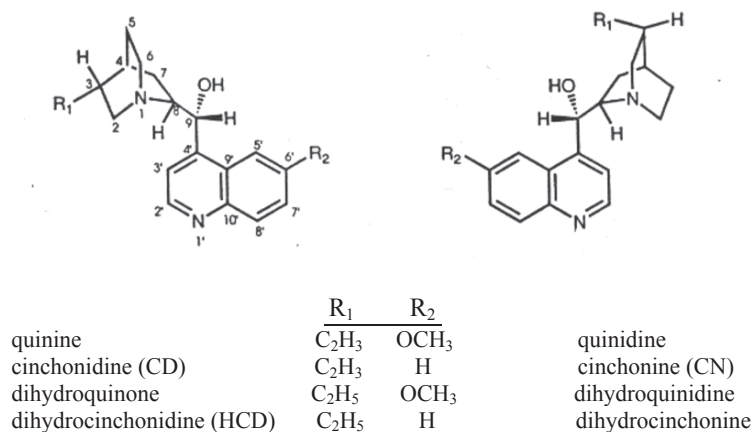


The authors <sup>116</sup> noted: "...This enantioselective catalysis should extend the scope of our strategy for tailored specific catalysts by the molecular imprinting method...". A review of these works exists <sup>116</sup>. Indeed, these results are of great interest, but it is necessary to note that Kaiser and Anderson <sup>117</sup> were unable to repeat the results with the benzamide imprinted silicas. Their failure probably was the result of a short lifetime for the specific properties of such Al-doped silica gels.

Heilman and Maier <sup>118</sup> also attempted to imprint silicas but were unable to obtain sufficient evidence for the connection of catalytic activity with imprinted sites.



**Scheme 1.5.**



**Scheme 1.6.** Structures of cinchona alkaloids.

Another promising development is the preparation of adsorbents which are capable of selective adsorption of enantiomers and which possess the ability to resolve racemates. Along these lines, Curti and Colombo <sup>119,120</sup> prepared a silica gel adsorbent formed in the presence of (1S)-(+)-10-camphorsulfonic acid (Scheme 1.5.) and resolved on this adsorbent the same racemic acid with

an *ee* of 30%, and also they resolved the racemic mandelic acid with an *ee* of 10%. Beckett and coworkers<sup>121,122</sup> found selective adsorption of cinchona alkaloids and morphine on specific formed silica gels.

For elucidation of results the authors accepted the theory of "Fingerprints". Indeed, silica formed with alkaloids reveals a greater capacity for the same alkaloid in comparison to a control adsorbent without the imprinting molecules, and silica formed with quinine adsorbs more quinine and cinchonidine, more quinidine.

Adsorbate <u>adsorbent</u>	Control	Silica formed <u>with Quinine</u>	Silica formed <u>with Quinidine</u>
Quinine	146	394	196
Quinidine	142	232	220
Cinchonine	167	218	
Cinchonidine	200	190	

**Table 1.9.** Effect of structure of adsorbate molecule on the stereospecific adsorption on silica gels formed in the presence of quinine and quinidine (values at an equilibrium concentrations  $20 \cdot 10^{-5}$  mol/kg adsorbent) (modified data adapted from Beckett et al.<sup>122,123</sup>).

But Maier and coworkers<sup>123</sup> could not obtain positive results for stereoselective adsorption. Silica gel was imprinted with chiral 2-(4-MeOPh)-3,3-dimethylbutan-1-ol, but after its removal from the matrix the resulting imprinted silica gel was unable to resolve the same racemic mixture of the imprinting compound.

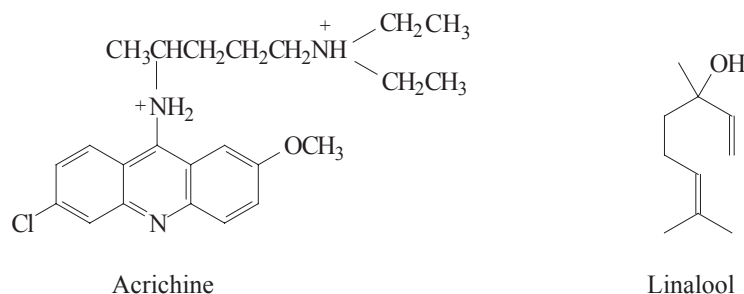
In the 1960's Klabunovskii and coworkers<sup>124,125,126,127,128</sup> expanded the concept of chiral recognition for preparing imprinted silicas originating from chiral alkoxysilanes followed by hydrolysis. They used tetra(2-methylbutoxy)silane as a templating agent to induce chirality at the inner and outer surfaces of silica gel. By this method the start of action of forming the specific chiral center more closely resembles the formation of the polymeric net of silica. During the process of formation of the active surface of silica the following factors can effect the results:

1. the chiral structure of the original silane
2. the optically active intermediates formed during partial hydrolysis
3. the optically active alcohol formed in full hydrolysis<sup>126</sup>.

A number of optically active menthoxybornyloxy-2-methylbutoxysilanes<sup>125</sup> and polymethoxyalkyl- and polycarbmenthoxysiloxanes were obtained by hydrolysis of silanes<sup>127</sup>. Polymers incorporating the menthoxy group were thermostable up to 200 °C.

The hydrolysis of (+)-(2-methylbutyl)trichlorosilane results in an optically active polymer, of which optical rotatory dispersion showed the absence of any contribution of the general polymer chain to the general optical rotation<sup>129</sup>. By hydrolysis of tetra(2-methylbutoxy)silane with full removal of the chiral group a specific silica gel was prepared<sup>128</sup>. The use of a MacBain quartz spring balance was used to measure adsorption isotherms. The adsorption of the racemic- and (+)-2-butanol vapors gave 23.8% excess more for the racemic than for the (+)-isomer, both at saturation and in a monolayer. This increase in adsorption of the racemic 2-butanol in comparison with the (+)-isomer was explained by its smaller molecular volume. Silicas formed in the presence of (+)-tartaric acid, (+)-mandelic acid, or (+)-Na tartrate proved to be less selective. Similar results were obtained in selective adsorption of *sec*-butylamine on specific formed silicas<sup>129</sup>.

Patrikeev, Balandin, Klabunovskii and coworkers<sup>130</sup> used silica gel formed in the presence of colonies of the soil bacteria, *Bacillus mycoides*, that revealed "right" and "left" spiral forms. These "chiral" silica forms relate differently towards the optical isomers of some poisons, for example, (+)- and (-)-acrichine. On silica formed in the presence of "right" and "left" forms of *Bacillus mycoides* the adsorption of (+)- and (-)-linalool was measured in vacuum on MacBain quartz spring balance. Silica formed in the presence of the "left" *Bacillus mycoides* colony adsorbed 8 times more (-)-linalool than (+)-linalool<sup>131</sup>.



**Scheme 1.7.**

Another concept of chiral molecular imprinting was developed by Wulff and colleagues<sup>131,132,133</sup> who used an organic polymer network as a matrix instead of silica. The main difference from all former methods consists of a template copolymerized and then removed to give a cavity in the polymer with highly specific binding sites rather than some sort of shape, such as a "fingerprint". This area of research is very promising, has grown rapidly<sup>94-97,132</sup>, is used in chromatography, and is used for selective adsorption and for selective catalysts<sup>133,134</sup>. Thus, the imprinting in a polymer was made with the chiral complex [Rh-{(R)-PhMeCHOH}]. On that polymer the hydrogenation of

PhCOEt yields 1-phenylpropan-1-ol with an *ee* of 8% and 10% conversion  
134,135

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