# Synthesis and stabilities of the basic copper(II) chlorides atacamite, paratacamite and botallackite

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## Abstract

Strictly reproducible syntheses of the trimorphs of composition $Cu_2Cl(OH)_3$, atacamite, paratacamite, and botallackite, have been developed. In syntheses involving direct precipitation, or reaction of aqueous solutions with solid phases, reliable results are obtained only if the temperature and time of reaction are carefully controlled. Botallackite, the rarest of the naturally occurring trimorphs, is a key intermediate and crystallizes first under most conditions; subsequent recrystallization of this phase to atacamite or paratacamite, or of the latter from the former, depends upon the precise nature of the reaction medium. The crystallization sequence indicates that paratacamite, as has long been suspected, is the thermodynamically stable phase at ambient temperatures. Spertiniite, $Cu(OH)_2$, can be reproducibly synthesized via one route in the non-commutative titration of aqueous copper chloride with aqueous sodium hydroxide solutions.

KEYWORDS: synthesis, stability, copper(II) chlorides, atacamite, paratacamite, botallackite.

## Introduction

BASIC copper(II) chloride of stoichiometry $Cu_2Cl(OH)_3$ is found as three naturally occurring phases, botallackite (monoclinic), atacamite (orthorhombic), and paratacamite (rhombohedral); all three crystal structures have been described (Wells, 1949; Fleet, 1975; Voronova and Vainshtein, 1958; Hawthorne, 1985). World-wide occurrences of atacamite and paratacamite have been reported (Frondel, 1950) and while perhaps their most notable deposits are in oxidized zones of base metal ores in arid climates (Bandy, 1938; Palache *et al.*, 1951), they are certainly not confined to such environments. Botallackite, on the other hand, is quite rare, although it was recognized as a new species more than a century ago (Church, 1865). As far as naturally developed oxide zones are concerned, it has been reported from the Botallack mine (Wheal Cock workings) in Cornwall, UK, where it was associated with atacamite and paratacamite (Kingsbury, 1964). These workings were located below the seabed, and chloride ion in seawater percolating through the ores was responsible for the crystallization of the phase. It has also been reported from Cligga Head, Cornwall (Embrey, 1957).

However, two other occurrences are worth noting. Gettens and Frondel (1956) reported botallackite as a major product of the corrosion of a bronze archaeological object which had been exposed to high chloride ion concentrations. Similarly, the mineral has been observed as a phase in the Laurium lead slags which have been a contact with seawater (Schnorrer-Kohler *et al.*, 1982).

A number of studies of the basic copper chlorides have been undertaken (Garrels and Stine, 1948; Garrels and Dreyer, 1952; Oswald and Feitknecht, 1964; Walter-Levy and Goreaud, 1969; Sharkey and Lewin, 1971, 1972; Woods and Garrels, 1986*a*) with a view towards explaining the stabilities of the trimorphs with respect to each other and to other commonly occurring copper(II) minerals, their syntheses, and their development as corrosion products on archaeological copper, bronze and brass objects. Woods and Garrels (1986*b*) have suggested that the occurrence of atacamite, paratacamite, and botallackite, among other species, may be used as an indicator of geochemical environment.

Despite this substantial body of research, however, several inconsistencies and gaps in the chemistry of the system have remained. It has not been certain, for instance, which of the species atacamite or paratacamite is the thermodynamically stable phase at room temperature. In addition, it has been noted that a number of

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reported synthetic procedures give apparently inconsistent results (Sharkey and Lewin, 1971, 1972; Tennant and Antonio, 1981). It has been suggested that the rate of stirring of reacting mixtures influences the crystallization of one or other of the three phases.

These observations, together with the reports concerning the non-commutative nature of the reaction of aqueous copper(II) chloride and sodium hydroxide solutions (King and Cooper, 1965; White, 1986), prompted us to re-examine several syntheses of botallackite, atacamite and paratacamite. Our results, reported below, indicate that the apparent inconsistencies mentioned above may be simply explained, and that all three above-mentioned basic copper(II) chloride minerals may be reproducibly synthesized. Conditions relevant to the crystallization of the rare mineral spertiniite, $Cu(OH)_2$, have also been elucidated.

## Experimental

Phases were identified in the first instance by X-ray powder diffraction methods, using the data in the JCPD powder file. Diffraction patterns were recorded using a Debye-Scherrer camera of 360 mm circumference and Cu-$K\alpha$ radiation using fine-grained material directly from the synthetic experiments. Subsequently, it was found that IR spectroscopy could be used reliably for identifications, even when several phases were present in admixture. IR spectra were measured in Nujol mulls or KBr discs (caution: excessive pressure should not be used, so as to avoid Br substitution or recrystallization)[1] using a Perkin Elmer 783 spectrophotometer. Absorptions were compared with those reported by Tennant and Antonio (1981), by reference to X-ray authenticated samples. Botallackite is easily recognized using this method, especially by the presence of characteristic absorptions at 3518 and 702 $cm^{-1}$ which are well removed from any modes observed for atacamite and paratacamite. Subtle intensity differences in the latter two phases associated with nearly overlapping IR modes are evident. Our spectra were calibrated for these effects by reference to the IR spectra of X-ray authenticated hand-picked samples (large crystals) of atacamite and paratacamite (National Museum of Wales specimens NMW 77.35G.M26 and NMW 83.41G.M4098, respectively). Solids from synthetic reaction mixtures were isolated by filtration on glass sinters at the pump. They were awashed quickly with water, then acetone, and dried *in vacuo* over silica gel at room temperature.

Synthetic brochantite, $Cu_4SO_4(OH)_6$, and malachite, $Cu_2CO_3(OH)_2$, were prepared by the methods of Woods and Garrels (1986*a*). Both were checked for purity using powder diffraction methods and thermogravimetric analysis using a Stanton Redcroft TG 750 thermobalance. All other reagents were of analytical grade. Sheet copper was cleaned using the method of Sharkey and Lewin (1971). Copper concentrations in some experimental solutions were measured by AAS using a Varian AA-275 spectrophotometer. Measurements of pH were performed using a Radiometer PHM85 pH meter fitted with a Radiometer GK2401C combination electrode. The temperature of the reaction mixtures was maintained at ±0.5 °C by the use of a Grant FH15 circulating water bath. For reactions carried out between 0 and 20 °C, this apparatus was used in conjunction with a Grant circulating cooling unit.

Species distributions in aqueous solution at 25 °C were calculated using the computer programme COMICS (Perrin and Sayce, 1967) with equilibrium constants taken from Smith and Martell (1976) and Long and Angino (1977) for copper(II) hydoxide and chloride complexes. Corrections for ionic strength were made using the form of the Debye-Hückel equation as expressed by Turner *et al.* (1981) and by extrapolation of the higher ionic strength data of Smith and Martell (1976).

## Results and discussion

*Direct precipitation experiments.* When aqueous NaOH solutions are added to aqueous $CuCl_2$ solutions (both 0.05, 0.1, 0.2, 0.4 or 0.5 mol $dm^{-3}$) at either 0 or 25 °C, whether with vigorous stirring or not, the only solid phase that could be isolated is pure paratacamite.[1] This was the case irrespective of the extent of reaction up to the 3:2 ($OH^-:Cu^{2+}$) end-point, and the observations are entirely in accord with those of previous workers (Oswald and Feitknecht, 1964; Sharkey and Lewin, 1971). With results of other syntheses in mind (*vide infra*), solids isolated at short reaction times, particularly at 0 °C, were carefully examined by IR and powder diffraction methods for the presence of any other phase; none was found. We estimate that any species in these runs could have been detected at the 1% level.

However, a different distribution of reaction products is found when the direct titration is carried out at lower copper ion concentrations. Titration of a $4.25 \times 10^{-3}$ mol $dm^{-3}$ aqueous $CuCl_2$ solution with aqueous NaOH (0.05 mol $dm^{-3}$) at 18°C produced botallackite, if the solid phase was isolated immediately after the 3:2 end-point was reached. If the botallackite is left in contact with the mother liquid, quite rapid recrystallization to paratacamite ensues.

The recrystallization was found to be sensitive to the rate of addition of hydroxide and to the concentration of chloride ion in solution; the latter was varied by addition of known amounts of NaCl. At chloride ion concentrations higher than

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[1] At the pressures used, 1.5 tonnes $cm^{-3}$, to prepare the KBr discs, no alteration of any phase into any other was observed.

[1] Very rapid addition of base gives a transient pale blue precipitate which rapidly recrystallizes.

$0.2\,\mathrm{mol\,dm^{-3}}$, both paratacamite and atacamite are found to recrystallize from the initially-formed botallackite. The atacamite itself recrystallizes to paratacamite if the initial chloride concentration is less than $0.4\,\mathrm{mol\,dm^{-3}}$. Otherwise, with negligible copper ion remaining in solution, atacamite is stable over longer periods (>1 week). We comment further on these stability relationships below.

The non-commutative nature of the direct precipitation method using higher starting copper concentrations has been noted by other workers in the past (King and Cooper, 1965; White, 1986), the former reporting that $Cu(OH)_2(s)$ is formed when aqueous solutions of a Cu(II) salt and NaOH are mixed together with $OH^-$ in excess. In this connection, it is worth noting that Sharkey and Lewin (1971) reported that equal volumes of equimolar aqueous $CuCl_2$ and NaOH always gave paratacamite irrespective of the order of addition; in these experiments excess copper(II) ion is always present. White (1986) reported that, on the other hand, aqueous NaOH solutions could be titrated with aqueous $CuCl_2$ up to a 1:2 end-point corresponding to the precipitation of $Cu(OH)_2(s)$.

All of these observations require some qualification. Temperature, reaction time and ratios of reactants may be varied to give several results. Titration of excess aqueous $OH^-$ with $CuCl_2(aq)$ gives, initially, a deep blue precipitate. At elevated temperatures this ultimately recrystallizes to tenorite, CuO. The blue material persists at 25 °C, and for longer at 0 °C, and may be isolated by filtration and drying over silica gel at room temperature. Analysis of the product shows it to be normal copper(II) hydroxide, $Cu(OH)_2$(l.c.) (The calculated analysis for Cu(OH) is: CuO, 81.5; $H_2O$, 18.5%. The actual analysis is: CuO, 81.1%; $H_2O$, 18.4%; Cl, 0.5%). The material contains minor chloride, as does the naturally occurring phase, spertiniite (Grice and Gasparrini, 1981). The true nature of the precipitated phase was confirmed by X-ray powder diffraction methods. Spertiniite is formed up to the 1:2 end-point of the titration. However, if the rate of addition of $CuCl_2(aq)$ is slow, and the mixture is allowed to come to equilibrium, as monitored by cessation of pH change, paratacamite is found to form. Titration under these conditions proceeds to the 3:2 ($OH^-:Cu^{2+}$) end-point. Addition of aqueous $CuCl_2$ in excess of the 1:2 end-point accelerates the recrystallization of spertiniite to paratacamite left in contact with the aqueous phase. Notably, if the precipitate is isolated soon after the end-point is passed, both paratacamite and botallackite are found to be present in the mixture. The latter phase quickly recrystallizes to the former even at 0 °C. Spertiniite is a very rare mineral. Solutions from which it was observed to have crystallized had a pH of about 9.2. Its rarity is in accord with the above observations in that the order of mixing of aqueous solutions bearing $Cu^{2+}(aq)$ and $OH^-(aq)$ is important and that given even short times in contact with reacting solutions it is replaced by other thermodynamically stable phases.

*Corrosion of metallic copper.* The corrosion of cleaned copper foil in various solutions was followed using a procedure modified from that of Sharkey and Lewin (1971). Copper(II) chloride solutions (0.01–0.07 M in increments of 0.01 and 0.1–0.05 M in increments of 0.1) were equilibrated at 0, 7, 25 and 40 °C in a thermostatted water bath prior to the addition of Cu foil. The pH of the reaction mixtures was monitored as was the total concentration of copper in solution by AAS, the latter in separate experiments. As soon as a precipitate was observed to have formed, the copper foil was removed from solution, and the precipitate isolated in the usual way. In other experiments, the mixtures were allowed to react for longer times (up to one week), with the precipitate being sampled periodically.

Variation of temperature in these reactions is found to have no effect upon the nature of the phase which is finally formed during one week. Recrystallization phenomena are, as expected, faster at higher temperatures, but the sequence of crystallization is the same for any concentration of aqueous copper(II) chloride.

In similar experiments, Sharkey and Lewin (1971) reported that at low concentrations of $Cu^{2+}(aq)$ [$Cl^-(aq)$] paratacamite was the only phase observed. At about 0.1 M ($Cu^{2+}$) atacamite was the major product and that, at higher concentrations, the proportion of paratacamite increased. These experiments were carried out at 25 and 100 °C and solids were sampled after 46 hours reaction. In the light of our experience, these results too require some qualification.

The first phase to crystallize in all cases is botallackite. Recrystallization to other phases then occurs, depending on temperature and concentration. No botallackite is detectable in any of these systems after 24 hours. At $CuCl_2(aq)$ concentrations from 0.01 to about $0.06\,\mathrm{mol\,dm^{-3}}$, the initially-formed botallackite recrystallizes to paratacamite without the formation of observable quantities of atacamite. At higher concentrations, botallackite recrystallizes to atacamite. Atacamite is most stable at an initial concentration of $CuCl_2(aq)$ of about $0.1\,\mathrm{mol\,dm^{-3}}$; no further reaction is observed in such solutions over one week at 25 °C. However, at higher concentrations, atacamite recrystallizes in turn to paratacamite, with the rate of the transformation increasing with increasing concentration. This fact explains the observations of Sharkey and Lewin (1971), who sampled at constant reaction time.

These recrystallization phenomena are also sensitive to increasing chloride ion concentrations. Aqueous copper(II) chloride solutions at the same concentrations as those given above up to 0.2 M were made 0.5 M in chloride ion by addition of NaCl. The same sequences of crystallization–recrystallization were observed, except that the addition of excess NaCl causes the recrystallization of atacamite to paratacamite to proceed much more slowly. In general, it thus appears that $Cu^{2+}$(aq) promotes, and $Cl^{-}$(aq) inhibits this transformation. Such a simple conclusion may be complicated by the formation of complex species in solution (*vide infra*), but it is important to note that solution species are significant; Sharkey and Lewin (1972) could not effect the recrystallization of atacamite to paratacamite in water alone, even at somewhat elevated temperatures (120 °C). On the other hand, Oswald and Feitknecht (1964) found that atacamite converts to paratacamite with heating in a sealed tube at 200 °C for three days.

The results of our solution experiments indicate conclusively that paratacamite is the thermodynamically stable phase from zero to 40 °C, the range generally appropriate for oxidizing sulphide ores and the corrosion of metallic artefacts. Woods and Garrels (1986*a*) have noted that paratacamite and atacamite have apparently trivial differences in stability. Their experimental work concerning paratacamite led to a value of $-1341.8\,kJ\,mol^{-1}$ for $\Delta fG°$ (298.2K, paratacamite, s), identical with that for atacamite as reported by Barton and Bethke (1960), and comparable with data tabulated by others (Naumov *et al.*, 1974; Wagman *et al.*, 1982). For the purposes of discussing the relative stabilities of the copper(II) hydroxychlorides, we see no reason for not adopting the above figure, for the free energy of formation of paratacamite, especially since the crystallography of the phase was well characterized.

With this in mind, one may profitably employ the results of a study by Sharkey and Lewin (1972) on the thermal properties of the copper hydroxy chlorides. In particular, they report enthalpies of dehydration of 126.0. 119.3 and $106.8 \pm 1.8\,kJ\,mol^{-1}$, for paratacamite, atacamite and botallackite, respectively. As pointed out by the above authors, since $S°$ values for the dehydrations arise primarily from the formation of gaseous $H_2O$, this parameter does not impinge to any great extent on considerations of relative stability. That is, differences principally involve $\Delta H°$ values. Therefore, using the above results we may calculate $\Delta fG°$ (298.2 K) values of $-1335.1$ and $-1322.6 \pm 3.6\,kJ\,mol^{-1}$ for atacamite and botallackite, respectively. The result for atacamite is comparable with that given by Wagman *et al.*, (1982). Reference to the crystal structures of the three polymorphs (Wells, 1949; Fleet, 1975; Voronova and Vainshtein, 1958; Hawthorne, 1985) suggests that differences in hydrogen bonding in the minerals could account for differences in thermodynamic stability. Weak hydrogen bonding is noted for botallackite, the least stable phase, between hydroxyl oxygen and chlorine atoms of adjacent $[Cu_2(OH)_3Cl]$ octahedral edge-sharing sheets are parallel to {100}. Such conclusions are reinforced by the results of IR spectral studies of the three minerals (Sharkey and Lewin, 1972, and refs. therein).

*Replacement reactions.* Some syntheses involving the reactions of brochantite, $Cu_4SO_4(OH)_6$, malachite, $Cu_2CO_3(OH)_2$, and calcite, $CuCO_3$, with aqueous copper(II) chloride and sodium chloride have been carried out. Reaction of brochantite with NaCl(aq) to form botallackite has been reported if the reaction mixture is not stirred (Sharkey and Lewin, 1972). Stirred solutions yielded paratacamite at 25 °C during 48 hours. Such results suggest again that the kinetics of recrystallization are important in this system, a fact that we have been able to confirm. Reactions of brochantite with aqueous NaCl (0.01, 0.02, 0.04, 0.05, 0.07, 0.1, 0.5 M and saturated) were carried out at 0, 25 and 50 °C, with stirring in all cases. Botallackite is the first-formed phase in all experiments at short sampling times. Isolation of the pure phase is best accomplished at lower temperatures. Recrystallization to paratacamite is observed for all concentrations without any atacamite being detected.

Exactly the same pattern of results has been found when malachite is substituted for brochantite in the above experiments. These experiments serve to identify botallackite as the intermediate observed by Woods and Garrels (1986*a*) during their emf titration of a malachite electrode with chloride ion, and suggest that botallackite is the intermediate phase reported in the related experiments of Feitknecht and Maget (1949).

Since the pioneering work of Garrels and Stine (1948), the reaction of solid $CaCO_3$ with aqueous solutions of $CuCl_2$ has been consistently reported as a reliable method for producing atacamite. however, Tennant and Antonio (1980) have observed botallackite to form in unstirred reaction mixtures over 48 hours (0.5 M $CuCl_2$), and

TABLE 1. Phases produced, pH and concentration data for experiments on the corrosion of copper in aqueous copper(II) chloride solution at 25°C.

| $[CuCl_2]$ aq, tot, initial/M | pH max | pH t=48h | Phases present[a] t=48h | Phases present t=1 week |
|---|---|---|---|---|
| 0.01 | 5.807 | n.d.[b] | para | para |
| 0.02 | 5.472 | 4.725 | para | para |
| 0.04 | 5.217 | 4.234 | para | para |
| 0.05 | 5.110 | 4.022 | para | para |
| 0.07 | 4.973 | 3.941 | ata | ata + para |
| 0.1 | 4.845 | 3.819 | ata | ata |
| 0.2 | 4.492 | 3.673 | ata + para | para |
| 0.4 | 4.198 | 3.381 | ata + para | para |
| 0.5 | 4.055 | 3.235 | ata + para | para |

[a] Ata = atacamite; para = paratacamite. [b] Not determined.

Feitknecht and Maget (1949) noted a similar result provided that alkali was a great excess. Experiments carried out in the present study (0.01–0.5 M $CuCl_2$) consistently yielded botallackite as the first solid phase, with subsequent recrystallization to atacamite. This latter phase was not found to recrystallize to paratacamite at 0 and 25 °C under any solution conditions during one week. This phenomenon might be due to the inhibition of the nucleation of the thermodynamically stable phase, paratacamite. Replacement of brochantite and malachite by basic copper(II) chloride in aqueous copper(II) chloride solutions (same conditions as for the reactions of metallic copper foils, above) again produced botallackite as the first phase. The pattern of recrystallization of this phase to atacamite, then paratacamite, or to the latter phase directly, followed the same course as was found during the corrosion of metallic copper in aqueous $CuCl_2$.

*Recrystallization phenomena.* Previous observations by other workers and the results reported here establish that paratacamite is the thermodynamically stable trimorph at ambient temperatures and that botallackite is the least stable polymorph. Crystallization of metastable phases and consequent transformations must be established under kinetic control and involve nucleation phenomena. Such phenomena are notoriously difficult to identify. A number of workers (Sharkey and Lewin, 1971; Woods and Garrels, 1986*a*, and refs. therein) have suggested that $[OH^-]/[Cl^-]$ ratios or concentrations of $CuCl^+(aq)$ and higher chloride complexes are perhaps important. Under all conditions examined here, botallackite crystallizes fastest, notwithstanding transient $Cu(OH)_2(s)$ formation in some cases, and $Cu^{2+}(aq)$ tends to promote and $Cl^-(aq)$ to inhibit the recrystallization of atacamite to paratacamite. Nucleation of paratacamite is apparently inhibited by the presence of $Ca^{2+}(aq)$ ions as suggested by experiments involving the replacement of calcite by basic copper(II) chloride species.

With these facts in mind, we have calculated some species distributions (see Experimental section for details) in solutions involving the corrosion of metallic copper in aerated aqueous copper(II) chloride solutions. The pH of these solutions rises initially as oxygen is reduced until the first solid phase, botallackite, begins to precipitate. Some relevant data are summarized in Table 1. During the course of these experiments, the total $Cu^{2+}$ and $Cl^-$ concentrations are not much changed, due to the limited extent of the overall reactions. The pH of the solutions then falls and stabilizes after about 48 hours. Maximum pH is reached at lower $[Cu^{2+}]$, $[Cl^-]$ concentrations, consistent with the solubility product of botallackite being exceeded.

Examination of selected parameters from the species distribution calculations using the COMICS programme (Table 2) indicates that there is no simple explanation for the recrystallization phenomena. With respect to the results outlined above, should certain solution species be important, then their concentrations would have to vary such that a maximum or minimum was achieved at $[CuCl_2]$, aq, tot equal to about 0.1 mol dm$^{-3}$. No single species fits this requirement, although

TABLE 2 . Equilibrium concentrations of selected species in solution calculated for experiments concerning the corrosion of copper in aqueous copper(II) chloride solution at 25°C.

| $[CuCl_2]$,aq,tot, initial/M | $[Cu^{2+}]_e$/M | $[Cl^-]_e$/M | $[CuCl^+]_e$/M | $[CuCl_2{}^o]_e$/M | $10^4[H^+]_e$/M [a] |
|---|---|---|---|---|---|
| 0.02 | 0.018 | 0.038 | 0.002 | b | 0.188 |
| 0.04 | 0.031 | 0.076 | 0.008 | b | 0.583 |
| 0.05 | 0.037 | 0.087 | 0.013 | b | 0.951 |
| 0.07 | 0.046 | 0.116 | 0.024 | b | 1.146 |
| 0.1 | 0.054 | 0.153 | 0.046 | 0.001 | 1.517 |
| 0.2 | 0.096 | 0.292 | 0.101 | 0.003 | 2.123 |
| 0.4 | 0.204 | 0.592 | 0.185 | 0.011 | 4.159 |
| 0.5 | 0.276 | 0.762 | 0.211 | 0.013 | 5.821 |

[a] Calculated without correction for ionic strength.

[b] These concentrations are negligible with respect to the species distributions for Cu(II) complexes.

the ratios $[Cl^-]/[H^+]$, $[Cu^{2+}]/[H^+]$ and $[CuCl^+]/[Cu^{2+}]$ at equilibrium do possess maxima or minima under the conditions employed during the corrosion of copper metal to produce the basic chlorides. Just which of several combinations of these parameters might be responsible for the sequence of recrystallizations and nucleations is unclear. However, it should be noted that examination of comparable data for the direct precipitation experiments at $4.25 \times 10^{-3}$ M total $Cu^{2+}$ shows the change to maximum stability of atacamite to coincide with significant rises in the ratios of $[CuCl^+]/[Cu^{2+}]$ and $[Cl^-]/[H^+]$ together with a reduction in that of $[Cu^{2+}]/[H^+]$. Botallackite nucleates the fastest under all conditions examined (when it does form), but the concentration of the dissolved species $CuCl^+$(aq), or of $CuCl_2{}^o$(aq), alone is not sufficient to explain the known sequences.

Finally, we should like to comment on the rarity in nature of botallackite. It recrystallizes quickly under most conditions to the more stable polymorphs and thus might only be preserved if solutions responsible for its crystallization are removed from any given system or dried out. It is no doubt an ephemeral phase. The occurrence of botallackite in Cornwall in the Wheal Cock workings of the Botallack mine (Kingsbury, 1964) is noteworthy. Botallackite was found as a recently-formed phase near a plugged breakthrough in the back of one of the workings which had been opened to the sea. Much paratacamite is now present in these and associated workings, as has been the case in the past, and the natural setting of the minerals is quite in accord with their chemical behaviour in the laboratory.

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