chemical analysis and the Raman data show that the hollandite crystals are interwoven with glasses of similar composition. In particular, no zone of silica or jadeitic compositions can be distinguished within the grains. The glass can thus either be interpreted as a back-transformation product of hollandite or as a residual liquid quenched during the post-shock pressure and temperature release. The rare occurrence of jadeitic pyroxenes at the rim of some hollandite + glass zones can represent the subsequent transformation (or back transformation) of hollandite into jadeite + SiO_2. However, we have not yet observed zones of SiO_2 composition near the jadeitic grains.

The present study confirms the conclusion of Liu (4) that compositions close to the $NaAlSi_3O_8$ end-member system can adopt the hollandite structure. The natural occurrence of hollandite with 8 mol% of $KAlSi_3O_8$ contradicts the work of Yagi et al. (8), who concluded that the maximum solubility of the $NaAlSi_3O_8$ component in the $NaAlSi_3O_8$-$KAlSi_3O_8$-hollandite solid solution is limited to 40 mol%. Because the temperature conditions during the shock event in the Sixiangkou meteorite are higher than the temperature range experimentally explored by these authors, the present observations indicate that this solubility is temperature dependent.

The occurrence of the liquidus pair majorite-pyrope$_{ss}$ + magnesiowüstite constrains their crystallization at pressures between 21 and 25 GPa and at temperatures between 2273 and 2373 K (22). The density of the phases with bulk $NaAlSi_3O_8$ composition increases in the following order: albite < $NaAlSi_2O_6$ (jadeite) + $2SiO_2$ (quartz, coesite, or stishovite) < hollandite < $NaAlSiO_4$ (calcium ferrite) + SiO_2 (stishovite) (4, 8). The discovery of hollandite close to the $NaAlSi_3O_8$ end-member puts additional constraints on the shock P-T conditions of the Sixiangkou meteorite. The absence of the assemblage $NaAlSiO_4$ (calcium ferrite structure) + $2SiO_2$-stishovite sets the upper pressure bound at 23 GPa (4, 8). These data suggest that the formation of the high-pressure assemblages in the shock-induced melt veins in the Sixiangkou meteorite took place at lower pressures but at higher temperatures than previously estimated for shock-induced melt veins in chondritic meteorites (13, 14).

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19. Pieces of the M'bale L6 chondrite have been pressurized to 22 GPa and 1500 K in a multianvil press [high-pressure facility at the Bayerisches Geoinstitut (Bayreuth, Germany)] in the stability field of $KAlSi_3O_8$-hollandite. Nearly pure $KAlSi_3O_8$-ortho-clase of the starting material has been transformed to a new phase, presumably $KAlSi_3O_8$-hollandite. The Raman spectrum of this phase (Fig. 2) is different from that of orthoclase, which is characterized by strong bands near 500 and 950 cm^{-1}, characteristic of stretching vibrations of SiO_4 tetrahedra. The Raman spectra of $KAlSi_3O_8$- and $NaAlSi_3O_8$-hollandite resemble that of stishovite [R. J. Hemley, H. K. Mao, E. C. T. Chao, Phys. Chem. Miner. 13, 285 (1986)]. The small difference in the Raman frequencies between $(Ab_{80}An_{12}Or_8)$- and $KAlSi_3O_8$-hollandite is accounted for by the small difference in cell parameters (see Table 3).
20. The x-ray facility used in this study includes a rotating anode generator (18 kW), a capillary collimating system, and a CCD area detector. The radiation from the rotating anode with a molybdenum target is filtered by a zirconium foil so that the intensity of $K\beta$ is 1% of that of $K\alpha$. The beam of initial size 1 mm by 0.5 mm is collimated to 0.1-mm diameter using the capillary system. A special collimator is used to reduce the size of the x-ray spot to 40 μm full width at half maximum. The diffracted x-rays were collected on a 512 by 512 pixels area detector. Data were acquired at fixed 2θ settings of 15, 25, and 30 and a sample-to-detector distance of 210 mm. Collection time in different points varied from 15 min to 12 hours. Settings of the detector were calibrated with three external independent standards (W, MgO, Al_2O_3) at each position of the detector. The sample disk was mounted on a 0.4-mm hole in a larger steel disk that was loaded onto the goniometer stage. We rotated the sample plate 30° from the initial position normal to the x-ray beam with a step of 1° in the ω axis during data collection. The position of the collimated x-ray beam penetrating through the hollandite grain was continuously monitored on a screen using a CCD camera.
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Green, Catalytic Oxidation of Alcohols in Water

Gerd-Jan ten Brink, Isabel W. C. E. Arends, Roger A. Sheldon*

Alcohol oxidations are typically performed with stoichiometric reagents that generate heavy-metal waste and are usually run in chlorinated solvents. A water-soluble palladium(II) bathophenanthroline complex is a stable recyclable catalyst for the selective aerobic oxidation of a wide range of alcohols to aldehydes, ketones, and carboxylic acids in a biphasic water-alcohol system. The use of water as a solvent and air as the oxidant makes the reaction interesting from both an economic and environmental point of view.

Traditionally, oxidations of alcohols are performed with stoichiometric amounts of inorganic oxidants, notably chromium(VI) reagents (1). These oxidants are not only relatively expensive, but they also generate copious amounts of heavy-metal waste. Moreover, the reactions are often performed in environmentally undesirable solvents, typically chlorinated hydrocarbons. In a constant search for cleaner ("greener") technologies, there is a definite need for catalytic oxidations that use dioxygen (O_2) or hydrogen peroxide as the stoichiometric oxidant (2). These oxidants are atom efficient (3) and produce water as the only by-product.

Although the advantages of using oxygen in alcohol oxidation are evident, reports on this particular subject are still scarce. Most

reports involve the oxidation of activated benzylic and allylic alcohols (4) or use the Mukaiyama co-oxidation method (5). Only recently have a few examples involving oxidations of nonactivated alcohols with O_2 been reported. Many examples of homogeneous systems make use of palladium (6), copper (7), or ruthenium compounds (8), typically in toluene as solvent. However, if these oxidations could be performed in water, they would be considerably safer, cheaper, and more environmentally friendly than many of the processes in use today (9). Moreover, when a water-soluble catalyst is used in a biphasic system, most products can be separated by simple decantation, and the catalyst solution can be recycled. In contrast, the use of an organic solvent, such as toluene, necessitates a tedious distillation and cumbersome recovery of the catalyst. Furthermore, the method is not suitable for products that have boiling points close to that of the organic solvent used (10). Despite the advantage of using water as a solvent, none of the catalyst systems mentioned here have been shown to operate in water. In fact, most reactions are performed under anhydrous conditions, which seems unpractical because, by definition, water is formed during the reaction. Development of a catalyst system that not only is stable toward water but is also completely soluble in this solvent seems highly desirable.

Supported noble metals, such as palladium or platinum on carbon, are known to catalyze the aerobic oxidation of alcohols in an aqueous medium, but the method is generally limited to water-soluble substrates, such as carbohydrates (11). Moreover, primary alcohols are oxidized to carboxylic acids, and one equivalent (1 equiv) of base is required. Herein we report an extremely effective aerobic oxidation of alcohols, both of activated and nonactivated hydroxyl groups, performed in water with a soluble
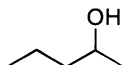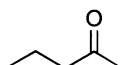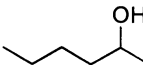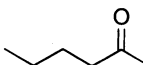
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Fig. 1. Aerobic oxidation of alcohols catalyzed by water-soluble PhenS*Pd(OAc)$_2$ (0.25 to 0.5 mole percent). R, alkyl, aryl.
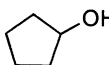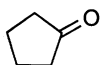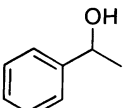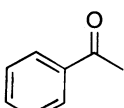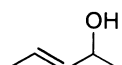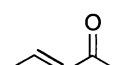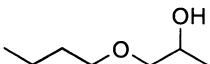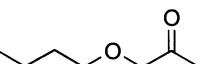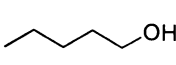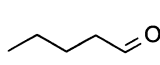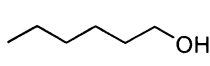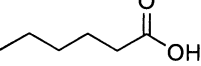
catalyst. The latter is a water-soluble palladium complex of bathophenanthroline disulfonate (PhenS*) (12) (Fig. 1).

Most alcohols (certainly those larger than C_4–OH) are only partly soluble in water, which gives a constant alcohol concentration in the aqueous phase and thus a constant reaction rate. For the smaller, more soluble alcohols such as 2-pentanol, cyclopentanol, or cyclohexanol, the initial turnover frequency is ~100 mmol/mmol per hour (13). This rate is about one order of magnitude faster than other aerobic oxidations of nonactivated secondary alcohols reported. Because 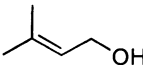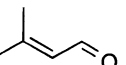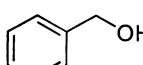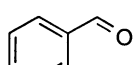the reaction rate is largely determined by the solubility of the alcohols, the reaction rate gradually decreases for higher alcohols, but even alcohols such as 2-octanol or 2-nonanol are oxidized at appreciable rates of 20 and 14 mmol/mmol per hour, respectively. Higher rates may be achieved for these alcohols through the addition of cosolvents or compounds such as alkanesulfonates or anthraquinone-2-sulfonate, which increase the alcohol concentration in the water phase. Nonactivated secondary alcohols show remarkably high reactivity; this is unexpected because others noted that some of the substrates given in Table 1 are notoriously difficult to oxidize (7).

The scope of the method is illustrated (Table 1) by the wide range of both primary and secondary allylic, benzylic, and aliphatic alcohols that can be oxidized in high conversions and selectivities. For example, with cyclopen-

Table 1. Conversion of primary and secondary alcohols. (All yields are for the pure, isolated products.) Conditions were as follows: 1° alcohol and 1-phenylethanol (10 mmol), 2° alcohol (20 mmol), PhenS*Pd(OAc)$_2$ (0.05 mmol), substrate/catalyst ratio of 200 to 400, water (50 g), NaOAc (1 mmol), pH ~11.5, 100°C, and 30-bar air pressure. Selectivity is based on the yield determined by gas chromatography with an external standard.

Substrate	Product	Time (hour)	Conversion (%)	Selectivity (%)	Isolated yield (%)
		5	100	100	90
		10	100	100	90
		5	100	100	90
		10	90	100	85
		10	95	83*	79
		10	100	100	92
†		15	98	97‡	90
		12	95	90§	80
		10	100	96‡	88
		10	100	99.8‡	93

*Ether (17%) was formed. †TEMPO (4 equiv to Pd) was added. ‡Acid was formed as the major by-product. §Hexanal (7%) and hexyl hexanoate (2%) were formed.
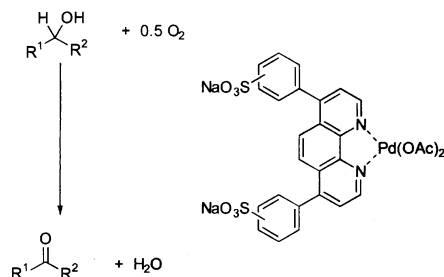
tanol, a turnover number of 400 was achieved to give cyclopentanone in 90% isolated yield (13). This reaction occurred without a substantial loss of activity or selectivity and with the option to reuse the catalyst (14). In the case of primary alcohol oxidation, a substrate/catalyst ratio of only 200 was used, because primary alcohols react more slowly than secondary alcohols for different reasons (15, 16).

The secondary alcohols were all oxidized selectively, although the "activated" 1-phenylethanol and 3-penten-2-ol react relatively slowly. The allylic and benzylic primary alcohols all reacted to form their corresponding aldehydes, whereas the nonactivated 1-hexanol reacted further to form hexanoic acid. Formation of this acid decreases the solution pH, and the reaction rate decreased. Adding TEMPO (the stable free radical 2,2,6,6-tetramethylpiperidinyl-1-oxyl) stops the reaction at the aldehyde. However, the reaction is slow, presumably due to coordination of TEMPO to the metal. Thus, the conversion of primary aliphatic alcohols may be directed to form either aldehydes or carboxylic acids. The latter product is especially interesting, because formation of a carboxylic acid from a primary alcohol with the oxidants known today is usually accompanied with the formation of 1 equiv of salt as a coproduct. The presence of an ether functionality (in butyl proxitol) does not affect the catalyst. Other functional groups, such as sulfides or amines, appar-

ently coordinate strongly to palladium, and no reaction was observed with alcohols containing these functionalities. Similarly, the double bonds in 3-penten-2-ol and 3-methyl-2-buten-1-ol presumably coordinate to palladium as in Wacker-type reactions, but these only slow the reaction down. However, Wacker-type products were not detected in these cases.

Mechanistic studies of olefin oxidations with this catalyst showed that, under neutral conditions, the catalyst precursor is a dimeric palladium species with two bridging hydroxy ligands (17). Increasing the pH values up to pH ~10 will yield a similar dimeric species with three bridging hydroxy ligands (18), apparently without changing the rate equation. The addition of sodium acetate (NaOAc) further increases the reaction rate. The reaction may also be carried out at neutral pH at only marginally lower rates. We propose that coordination of the alcohol to the metal center splits the dimeric precursor (Fig. 2). Next, a base abstracts a proton from the coordinated alcohol to form a palladium alcoholate species that subsequently undergoes β-hydride elimination to give the alkanone, water, and a zerovalent palladium species. Oxidation of the latter with O_2 gives a palladium peroxide. Reaction of this peroxide with 1 equiv of zerovalent palladium yields the starting palladium dimer. Reoxidation of Pd(0) seems to be facilitated by NaOAc, which avoids the

irreversible formation of a palladium mirror (19). A minimum of 1 mmol of NaOAc is recommended to avoid this palladium black formation.

If the reactions are carried out under pressure in an autoclave, the oxygen content of the gas phase does not seem to have any influence on the reaction, because the oxygen concentration in the aqueous phase is maintained at a high level. Therefore, catalytic oxidations could be carried out under an atmosphere of pure oxygen, of air, or of 8% oxygen in nitrogen. The latter is generally used in practice, because mixtures of 8% oxygen in an inert gas with organic compounds fall outside the explosion limits. In our case, the use of water as solvent increases the amount of inert material in the gas phase and allows for the safe use of air as the oxidant. Another benefit of the use of an autoclave is that loss of volatile substrates and/or products is avoided, which would occur on bubbling air through the solution at atmospheric pressure at 100°C.

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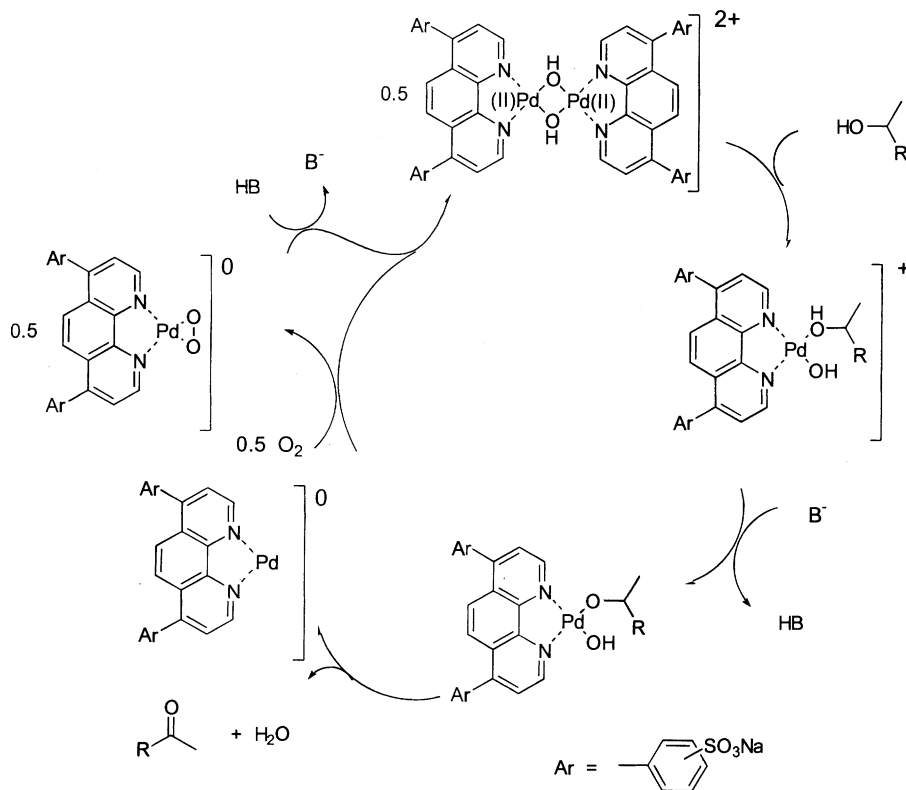
Fig. 2. The catalytic cycle proposed for alcohol oxidation with the aqueous-soluble PhenS*Pd(II) catalyst. Ar, aryl; B, base.

9. Typical reactions with the copper-phenanthroline system, see (7), were carried out in 800 ml of toluene at 80° to 90°C while bubbling through pure oxygen, which seems to breach safety regulations in most companies or institutions.
10. The boiling point of toluene is 110°C, which means that it is less suitable for the oxidation of, e.g., 1-pentanol, giving valeraldehyde (pentanal) with a boiling point of 103°C.
11. Because the catalyst is already in a separate solid phase, the alcohol must be solubilized; otherwise, reaction rates are very low. See, for instance, T. Mallat and A. Baiker, Catal. Today 19, 247 (1994).
12. Bathophenanthroline disulfonate, or 4,7-diphenyl-1,10-phenanthroline disulfonate, is a nontoxic pale yellow crystalline powder with no odor, CAS: [52746-49-3]. It is moderately soluble in water (>10% w/w). For further product information, see http://129.8.100.52/html/grad-lab/msds/d/4,7-diphenyl-1,10-phenanthroli0. It is commercially available from Pfaltz & Bauer (Waterbury, CT), Acros (Geel, Belgium), Alfa Aesar (Ward Hill, MA), Lancaster Synthesis (Windham, NH), or TCI (Tokyo). It is often used in biomedical kits to determine the iron content (non-heme) of serum or plasma in the diagnosis of iron deficiency anemia, hemochromatosis, and chronic renal disease through colorimetry. Sentinel Diagnostic (Milan, Italy) sells standard kits under the name of "Iron Bato."
13. The initial turnover frequency (in mmol/mmol per hour) is an indication of the speed of the reaction. It denotes the average number of substrate molecules (in mmol) that is converted by each mmol of catalyst in 1 hour. The turnover number (in mmol/mmol) denotes the average number of substrate molecules (in mmol) that 1 mmol of catalyst has converted during the course of the reaction.
14. In a reaction with 2-hexanol, the catalyst solution was recycled five times. Reactivity and selectivity remained >90 and 98%, respectively, of the initial values.
15. The catalyst solutions were prepared by stirring $Pd(OAc)_2$ (0.0112 g, 0.05 mmol) and PhenS* (0.0274 g, 0.05 mmol) overnight in water (50 ml) to give a clear yellow solution. Consecutively, $NaOAc \cdot 3H_2O$ (0.136 g, 1 mmol) and NaOH were added until pH ~11.5. The purity of the water and the chemicals used may dramatically influence the reaction rate.
16. Standard catalytic experiments were carried out in a closed Hastelloy C autoclave (175 ml). The autoclave was cooled and charged with the following catalyst solution: $PhenS*Pd(OAc)_2$ (0.05 mmol, 0.25 to 0.50%) in water (50 ml), alcohol (10 to 20 mmol), and internal standard (n-heptane, n-octane, or n-dodecane). The autoclave was pressurized with air and heated to 100°C (30 bar) until the reaction was complete. After reaction, the autoclave was cooled to room temperature and depressurized, collecting any volatile material in a liquid nitrogen trap. The mixture was extracted with Et_2O (Et, ethyl), the organic layer was dried over $MgSO_4$, and a different external standard was added (n-dodecane or n-hexadecane). Samples were analyzed by ^1H nuclear magnetic resonance ($CDCl_3$, 300 MHz) and gas chromatography [a Varian Star 3400 instrument equipped with a carbowax column (50 m by 0.53 mm)]. Ether was used to extract the relatively small amount of alcohol (10 to 20 mmol) from the aqueous phase to obtain good recoveries and more reliable data. In a large-scale process, the aqueous phase would be recycled after decantation of the product, and the use of organic solvent would be superfluous.
17. For identification of the catalyst, see G. J. ten Brink, I. W. C. E. Arends, G. Papadogianakis, R. A. Sheldon, Appl. Catal. A 194–195, 435 (2000).
18. S. W. Wimmer, P. Castan, F. L. Wimmer, N. P. Johnson, Inorg. Chim. Acta 142, 13 (1988); J. Chem. Soc. Dalton Trans. 1989, 403 (1989).
19. A similar effect has been observed for chloride anions, see, for instance, J. H. Grate, D. R. Hamm, S. Mahajan, in Catalysis of Organic Reactions, J. R. Kosak and T. A. Johnson, Eds. (Dekker, Dordrecht, Netherlands, 1994), chap. 16, pp. 213–264.

Translation of the Edited mRNA for Cytochrome b in Trypanosome Mitochondria

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The type of RNA editing found in the kinetoplast-mitochondria of trypanosomes and related protozoa, involving uridylate insertions and deletions, creates translatable messenger RNAs (mRNAs) out of nonsense pre-edited RNAs by correcting encoded defects that vary from simple frameshifts to large "cryptic" regions. However, any evidence for translation of these mRNAs in the kinetoplast has been missing for decades. We identified a kinetoplast-encoded protein, apocytochrome b, whose mRNA is edited in the 5' region. The determined amino-terminal sequence of the protein coincides with the predicted sequence derived from the edited region, demonstrating that the cognate apocytochrome b mRNA is translated into a functional protein. This finding represents the first direct evidence for a functional translation system in the kinetoplasts.

In trypanosomes and related protozoa from the order Kinetoplastida, mRNAs for several kinetoplast-mitochondrial genes undergo the posttranscriptional process of RNA editing, where additions, and occasionally deletions, of uridylate residues in the pre-edited mRNA produce a corrected reading frame (1). Depending on the mRNA species, the extent of this process varies from repairing an encoded frameshift by inserting a few uridylate residues to creating an entire reading frame by the insertion of hundreds of residues (2, 3). Small transcripts, termed guide RNAs, serve as the templates for the enzymatic editing machinery by defining the sites of editing and the number of insertions or deletions (4–6).

The functional significance of RNA editing is not clear. Although it may represent a mechanism of mitochondrial gene regulation, no direct biochemical proof for translation of edited mRNAs has been found since RNA editing was discovered in trypanosomes more than a decade ago (2, 7). The kinetoplast DNA sequence studies showed that, similar to other mitochondria, it encodes components of the mitochondrial ribosomes and subunits of the respiratory complexes, such as cytochrome c oxidase subunits I, II, and III (respiratory complex IV), apocytochrome b (complex III), and adenosine triphosphatase subunit 6 (complex V) (8). These complexes were isolated and their subunit composition analyzed by protein microsequencing (9–11). All detected subunits turned out to be nuclear encoded, thus leaving the existence of kinetoplast-encoded proteins an open question. Because earlier attempts in several laboratories to demonstrate kinetoplast translation in vivo or to isolate kinetoplast ribosomes were unsuccessful (7), these results, taken together, might question the very existence of a functional kinetoplast system of translation. However, the predicted encoded polypeptides were extremely hydrophobic, often with an increased cysteine content, and these properties could make the detection difficult, most likely due to aggregation and abnormal electrophoretic migration. Here, we present a first identification of a kinetoplast-encoded protein, apocytochrome b, a subunit of cytochrome bc_1 (complex III, ubiquinol:cytochrome c oxidoreductase) that is translated from an edited mRNA.

In the trypanosomatid Leishmania tarentolae the mRNA for apocytochrome b is edited in the 5' region by insertion of 39 uridylate residues at 15 sites (Fig. 1) (12). The process creates 20 NH_2-terminal in-frame codons, including the initiation triplet AUG. The predicted polypeptide of 44.5 kD contains 63% nonpolar residues, making it extremely hydrophobic. The cytochrome bc_1 complex was purified from L. tarentolae kinetoplasts by chromatography on DEAE-sepharose (13, 14). The purified enzymatic complex had a specific activity of 81.6 mU/μg. The cytochrome b and c_1 spectra and the heme content were similar to a previously isolated complex from the related trypanosomatid, Crithidia fasciculata (9). Analysis of the enzyme from L. tarentolae by denaturing SDS-polyacrylamide gel electrophoresis (Fig. 2) revealed nine subunits, all of which are nuclear encoded (14), similar to the enzyme from C. fasciculata. These subunits include three bands in the "core protein" region (bands 1 through 3), the

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